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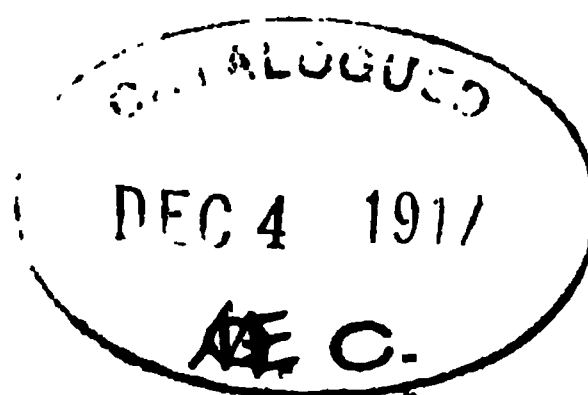
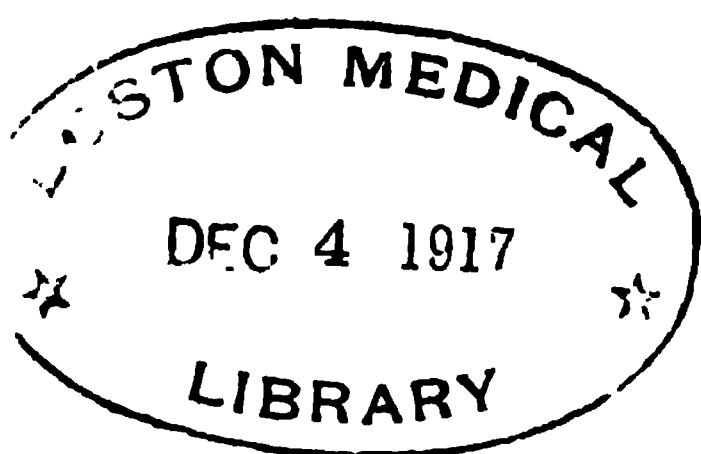
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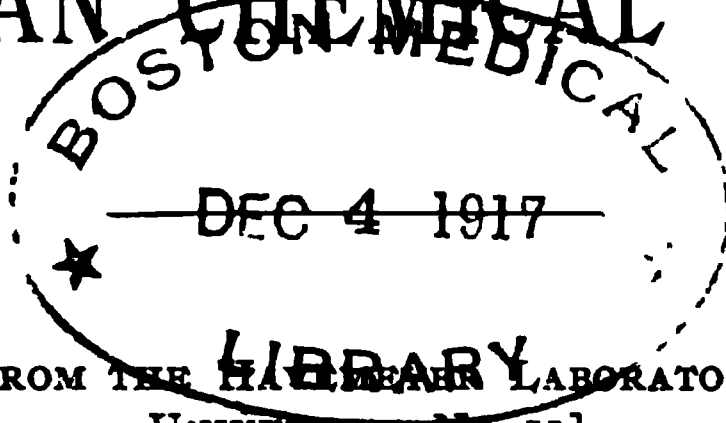
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## THREE ADDITIONS TO THE KOHLRAUSCH-OSTWALD CONDUCTIVITY METHOD.

BY J. LIVINGSTON R. MORGAN.

Received November 2, 1899.

THE Kohlrausch-Ostwald method for determining the electrical conductivity of electrolytes by means of an alternating current and telephone is very accurate and easy to use so long as the induction coil gives a clear high note. This condition, however, is not easy to fulfil, for, owing to the magnetization of the steel spring current breaker, the adjustment is soon lost. This objection holds for all coils which use steel for the vibrator whether in the form of a spring or wire. In preparing four sets of apparatus for conductivity so much difficulty was experienced in adjusting the coils that it was decided to find, if possible, another form of interruptor which would be free from this objection. As a result of this search an attachment was found which not only gives a clear high note, and allows of rapid adjustment, but which can be used for one set or for a number of sets of apparatus so that in the latter case all may be adjusted by one operation. Each piece of apparatus is

set up as usual except that the current breaker is removed from each coil, the interrupting being done for all in another room by an apparatus run by another source of electricity. This apparatus is a modified form of Professor M. I. Pupin's electrodynamic interruptor. The modifications referred to consist in the use of an electromagnet instead of the somewhat uncommon Weston permanent one, and in the interruption of a separate circuit instead of that which causes the string to vibrate. A

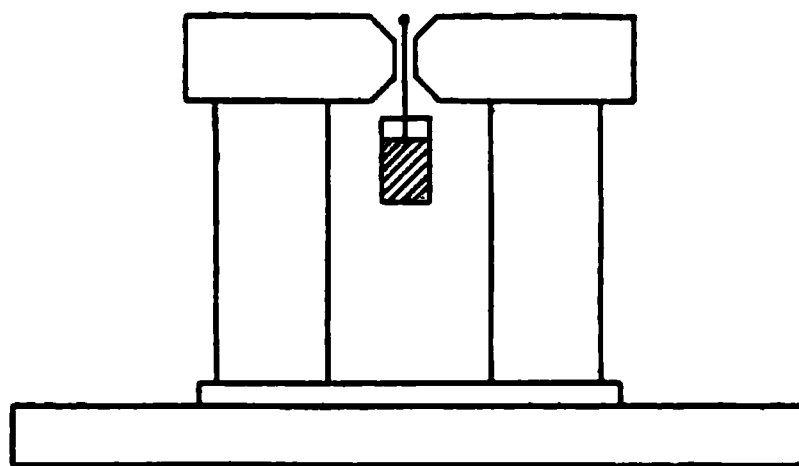


Fig. 1.

horseshoe electromagnet with special pole pieces (Fig. 1) is mounted vertically upon a base-board. On these pole pieces is fastened an oblong framework of brass, on the ends of which are screw devices to which the ends of a brass wire may be soldered and kept at any desired tension, between the pole pieces. Two mercury cups are placed the one in front and the other behind the magnet into each of which dips a short piece of amalgamated

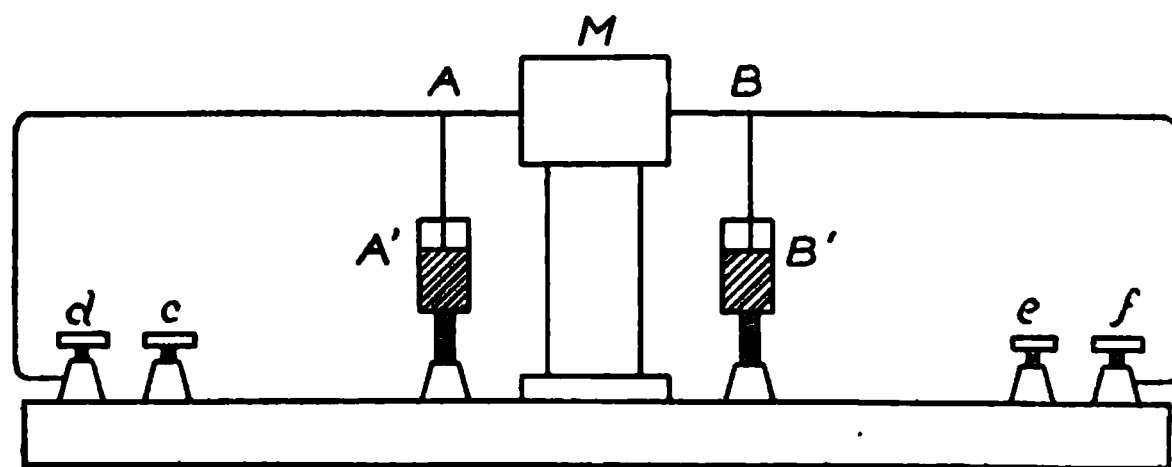


Fig. 2.—*c* is connected to *B'* and *e* to *A'* underneath the base. The current enters at *d* and *c* and one portion goes to the electromagnet *M* by wires not shown in the figure.

copper wire which is soldered to the brass wire. These mercury cups are so arranged upon screws that they may be raised or lowered so as to be in contact with the copper dippers. Fig. 2 shows the arrangement of the wire, cups and magnet with their connections. The current (three to six volts, taken from the

<sup>1</sup> *Am. J. Sci.*, 3d series, 45, p. 325 (1893).

electric light circuit or from storage cells) enters at the two binding-posts  $c$  and  $d$  and divides one portion going to the magnet through wires not shown in the figure, the other going from  $c$  through the wire to B, to the mercury at B' and back to  $d$ . When the current is flowing in this way, the wire is repelled by the magnet so that the contact at B' is broken but made again instantaneously by the tension of the wire. In this way the wire is retained in rapid vibration, and, if the cup A is properly adjusted, any battery circuit connected through  $e$ , A', A, and  $f$  will be interrupted. By connecting a Leclanché cell with an induction coil (with the breaker removed) through the two binding-posts  $e$  and  $f$  a rapidly alternating current is obtained and a clear high adjustable

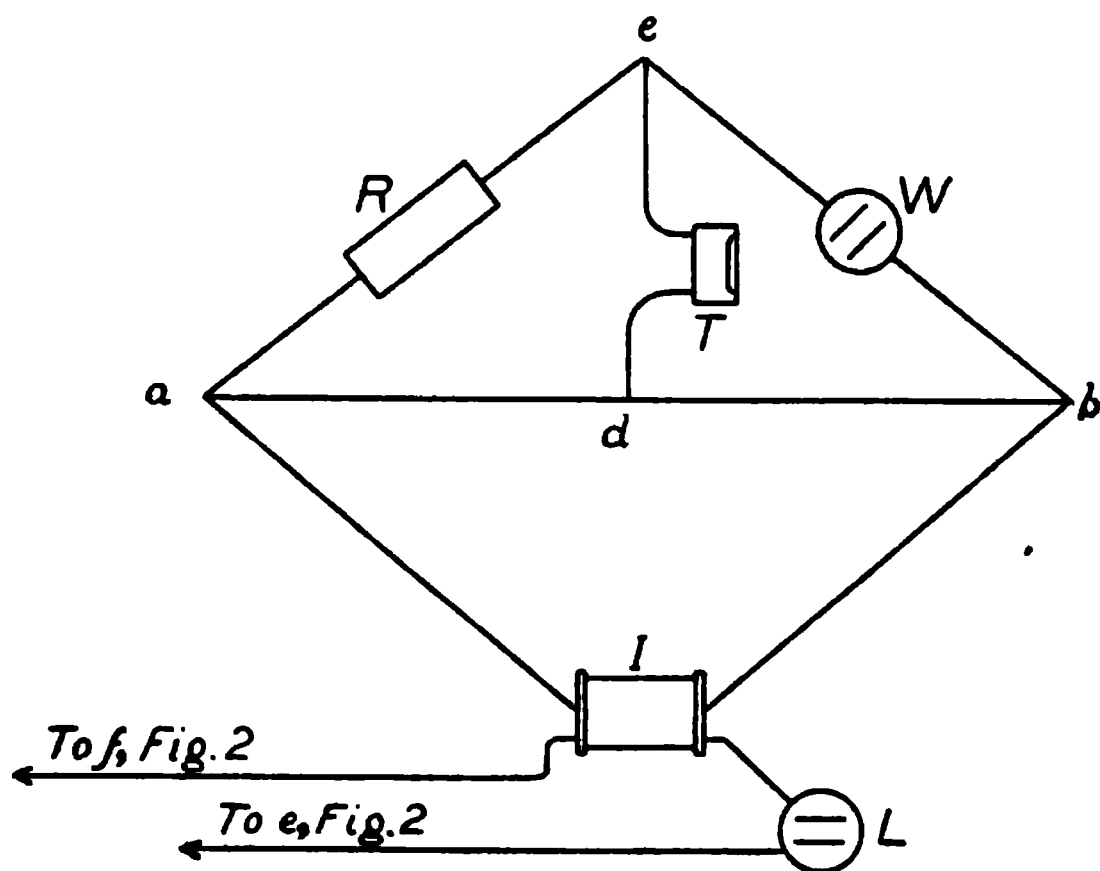


Fig. 3.— $R$  is the known resistance,  $W$  the electrolytic cell,  $I$  the coil,  $L$  the Leclanché cell and  $T$  the telephone.

note produced in the telephone. Fig. 3 shows the connections for a piece of apparatus set up in the way described so that no further explanation is necessary. Naturally any number of sets may be connected in this way through the interruptor, the same tone being obtained in all, and all may be adjusted at once. If the current necessary for the operation of the vibrator were not so great only one mercury cup would be necessary, but it has been found more satisfactory to simply interrupt the current from a single cell and thus to avoid heating and polarization effects at the electrodes. The arrangement described has been in use in

tension of water at various temperatures, the values of the "apparatus constant" were calculated for every  $10^\circ$ . These were found to change slightly but regularly.

The numerical results of the determinations are given in the following table and are represented graphically in Figs. I and II. Curves for  $0^\circ$ ,  $20^\circ$  and  $50^\circ$  only are drawn in Fig. I so as not to crowd too much. As it is, the right-hand parts of the curves practically coincide.

**SURFACE-TENSIONS OF MIXTURES OF SULPHURIC ACID AND WATER.**

**2.65 per cent.  $H_2SO_4$ .**

Tempera- ture.	Apparatus constant.	Distance be- tween ends of tubes in 0.025 inch.	Specific gravity.	Surface tension in dynes per cm.
$0^\circ$	1.260	56.39	1.021	73.60
$10^\circ$	1.266	55.71	1.019	72.69
$20^\circ$	1.273	54.83	1.017	72.02
$30^\circ$	1.278	54.04	1.015	71.13
$40^\circ$	1.283	53.12	1.013	70.07
$50^\circ$	1.290	52.13	1.011	69.01

**5.16 per cent.  $H_2SO_4$ .**

$0^\circ$	1.260	55.83	1.037	74.02
$10^\circ$	1.266	55.01	1.035	73.14
$20^\circ$	1.273	54.18	1.033	72.31
$30^\circ$	1.278	53.31	1.031	71.29
$40^\circ$	1.283	52.43	1.029	70.43
$50^\circ$	1.290	51.54	1.027	69.33

**11.87 per cent.  $H_2SO_4$ .**

$0^\circ$	1.260	54.02	1.081	74.75
$10^\circ$	1.266	53.46	1.078	74.10
$20^\circ$	1.273	52.86	1.075	73.48
$30^\circ$	1.278	52.15	1.072	72.58
$40^\circ$	1.283	51.32	1.069	71.52
$50^\circ$	1.290	50.41	1.066	70.45

**18.33 per cent.  $H_2SO_4$ .**

$0^\circ$	1.260	51.61	1.138	75.30
$10^\circ$	1.266	51.00	1.133	74.44
$20^\circ$	1.273	50.37	1.128	73.59
$30^\circ$	1.278	49.72	1.125	72.75
$40^\circ$	1.283	49.05	1.123	71.92
$50^\circ$	1.290	48.30	1.118	70.90
$60^\circ$	1.296	47.64	1.113	69.95
$70^\circ$	1.303	46.87	1.108	68.89

either one-half or one centimeter apart and have vulcanite knobs upon which to rest the fingers. As soon as the approximate reading is found with one key the block is moved until both keys when pressed give a tone of the same intensity; the middle point is then the true minimum. It is well to have the one key movable so that the distance between the contacts may be reduced as the point is reached. By the use of this arrangement it is possible to find the point within a small fraction of a millimeter and much less experience is necessary for accurate results than by the ordinary process.

### ON THE SURFACE-TENSIONS OF MIXTURES OF SULPHURIC ACID AND WATER, AND THE MOLECULAR MASS OF SULPHURIC ACID.

BY C. E. LINEBARGER.

Received October 25, 1899.

THE apparatus employed in making the measurements of the surface-tension was that described in a previous number of this Journal.<sup>1</sup>

The sulphuric acid used was Baker and Adamson's "chemically pure" (sp. gr. 1.84), and was found on analysis to contain 4.98 per cent. of water. This acid was mixed in varying proportions with water and the mixtures analyzed. The specific gravities of some of the mixtures were determined, but most of them were taken from Lunge and Isler's tables<sup>2</sup> and the corrections for temperature applied by means of the data given by Bineau.<sup>3</sup>

The thermostat consisted of a beaker filled with water and provided with a stirrer. A layer of heavy oil was poured over the water so as to prevent evaporation. Readings were taken (never less than three at the same temperature) at intervals of about 5°. These were plotted and a smoothed curve (which was approximately a straight line) drawn through them. From this curve, readings were taken at temperature-intervals of 10°, and these were used in calculating the surface-tensions.

Readings were taken in the same way with pure water, from which with the aid of Ramsay and Shields' data<sup>4</sup> on the surface-

<sup>1</sup> This Journal, 18, 514 (1896).

<sup>2</sup> *Ztschr. angew. Chem.*, 129 (1890). Landolt and Börnstein, 196.

<sup>3</sup> *Ann. chim. phys.* (3), 26, 123 (1849).

<sup>4</sup> *Ztschr. phys. Chem.*, 12, 433 (1893).

Tempera- ture.	Apparatus constant.	Distance be- tween ends of tubes in 0.025 inch.	Specific Gravity.	Surface tension in dynes per cm.
30°	1.278	27.02	1.755	63.70
40°	1.283	27.00	1.746	63.54
50°	1.290	26.99	1.737	63.48
60°	1.296	26.97	1.728	63.37
70°	1.303	26.96	1.718	63.19

95.02 per cent.  $H_2SO_4$ .

0°	1.260	23.63	1.843	58.26
10°	1.266	23.54	1.833	57.97
20°	1.273	23.46	1.824	57.76
30°	1.278	23.40	1.814	57.53
40°	1.283	23.39	1.805	57.43
50°	1.290	23.36	1.796	57.36
60°	1.296	23.31	1.786	57.28
70°	1.303	23.24	1.775	56.89

The foregoing data show that both the addition of water to sulphuric acid and of sulphuric acid to water increases the surface-tension of the liquids. The increase in the surface-tension of the acid even when but a small proportion of water is mixed with it is especially marked. The maximum surface-tension is observed when about equal quantities of the two liquids are mixed. It is also shown that certain mixtures of sulphuric acid and water, although of different percentage composition, may yet have equal surface-tensions. This is clearly brought out in the curves for mixtures containing 58.05 per cent. and 65.27 per cent., respectively, of the acid; the curves cross at an abscissa-value of about 22°. Besides this observed instance, other mixtures have a similar behavior. The limits of the values of their composition and surface-tensions may be learned by an inspection of the figures.

A noteworthy peculiarity of strong solutions of sulphuric acid in water is the slight influence that changes of temperature have upon their surface-tensions. The curves in Fig. 2 become more and more horizontal the greater the percentage of acid in the mixtures. From these low values found for the temperature coefficients, certain conclusions may be drawn as to the degree of molecular polymerization of pure sulphuric acid. It is true that no determinations were made of the surface-tension of the pure acid, but it seems reasonable to conclude that the regularity of



the curves would extend to the abscissa-value of the pure acid. Yet it is scarcely to be expected that anything like correct values for the surface-tension of the pure acid would be obtained by

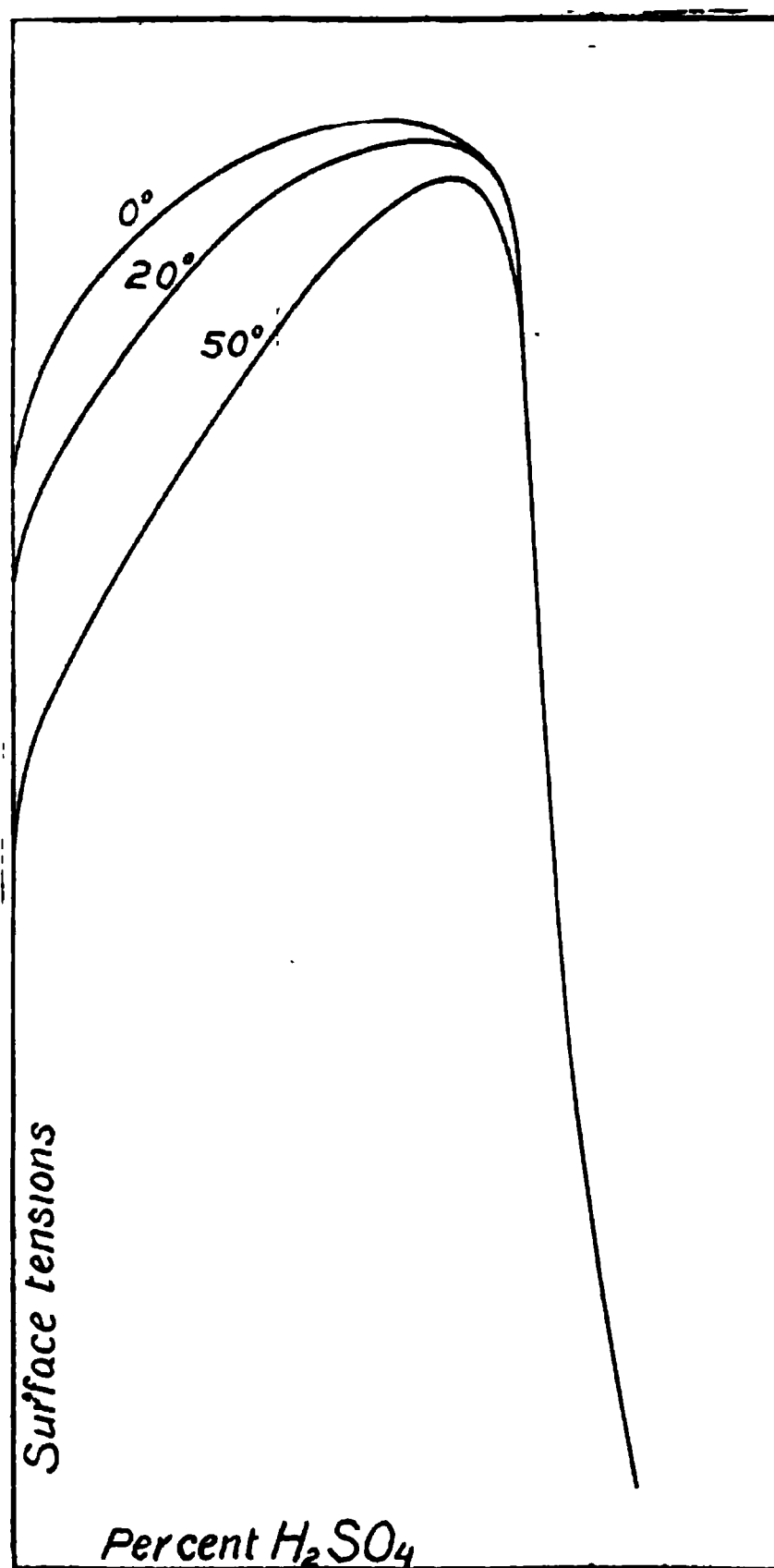


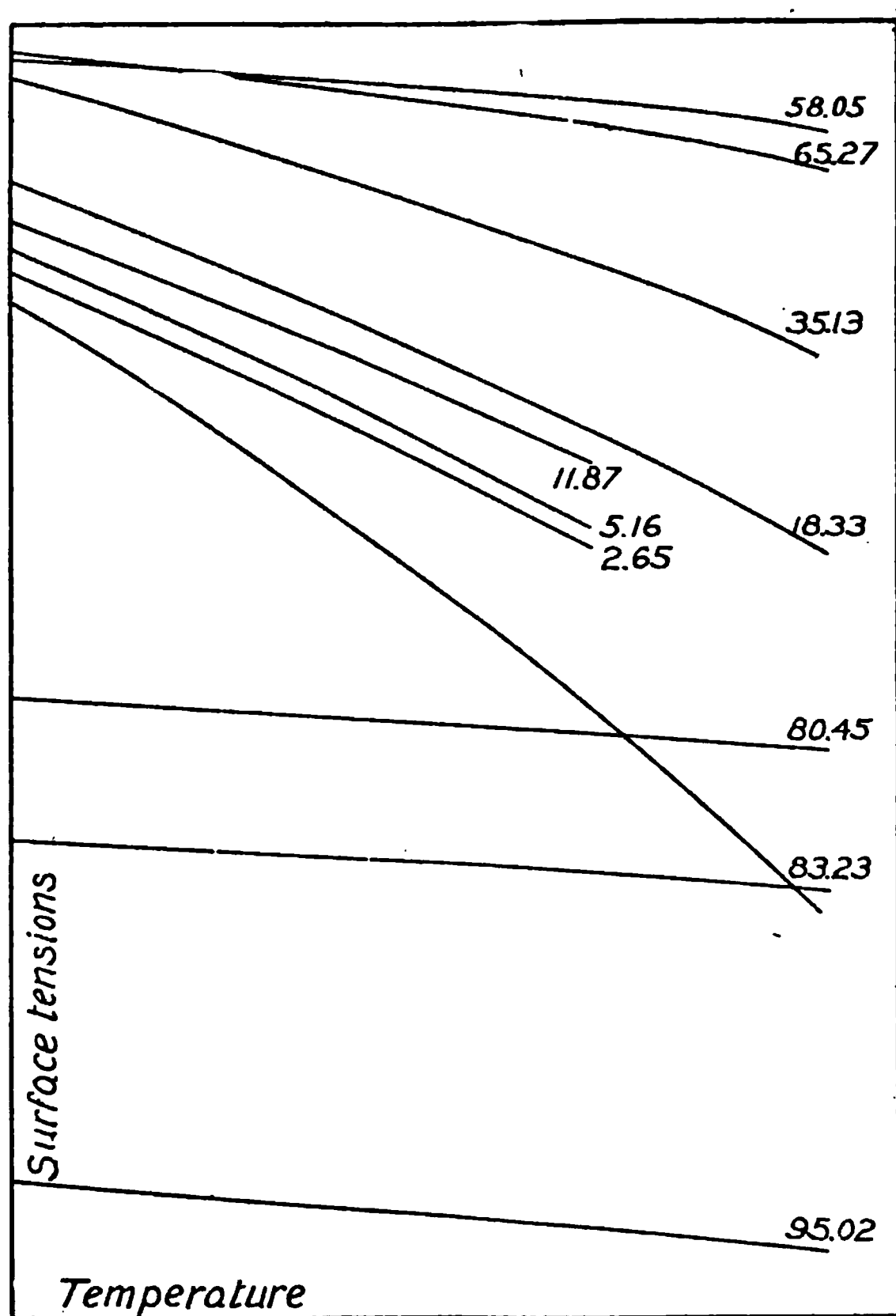
Fig. 1.

extrapolation, for the curves are too steep and close together. All that is legitimate to infer is that the pure acid has a small temperature coefficient with respect to its surface-tension.

Now according to the views of Ramsay and Shields<sup>1</sup> the degree of polymerization of a liquid may be estimated by means of the change of its molecular surface energy with the temperature. The smaller this is, the greater is the degree of polymeri-

<sup>1</sup> *Loc. cit.*

zation of a liquid's molecules. The small temperature coefficient of sulphuric acid points then to a high degree of polymerization; the molecular mass of its molecule must be several times 98, the molecular mass corresponding to the formula  $H_2SO_4$ . Ramsay



[Fig. 2.]

in a lecture before the Chemical Society of Paris<sup>1</sup> stated that he had found it probable that the molecule of sulphuric acid could be approximately represented by the formula  $(H_2SO_4)_n$ . If this be true, sulphuric acid has the most complex molecule of any liquid as yet examined in that regard, and this complexity of

<sup>1</sup> This was printed in the *Revue Scientifique* (4), 2, 1 (1894). No data or details seem to have been given in any of the journals devoted to the publication of chemical research.

molecular structure may account for many of the anomalous properties of mixtures of sulphuric acid and water.

The conclusion that sulphuric acid is molecularly polymerized to a very considerable extent would indicate in accordance with the views of Nernst<sup>1</sup> and Brühl<sup>2</sup> that the pure acid should have a large dielectric constant and high dissociative power. The specific inductive capacity of sulphuric acid has not been determined and no measurements of the electric conductivity of salts dissolved in it have been made. The electric conductivity of a concentrated acid may, indeed, be regarded as due to the ions of water, for the acid may be considered to be the solvent and water the dissolved substance. If the dielectric constant of pure sulphuric acid should be found to be larger than that of water, it seems in the light of the views of Nernst and Brühl quite natural to suppose that the acid would exert a not inconsiderable dissociative power on water. Still even in concentrated acid, the extraordinary dissociative power of water would assert itself, and the acid regarded as solvent would become dissociated into its ions in part. The circumstance that the acid may dissociate into more than two ions together with the probability that it is molecularly polymerized, complicates matters greatly.

The fact found by Kohlrausch<sup>3</sup> that a 10 per cent. solution of water in sulphuric acid presents a maximum of conductivity may perhaps be taken as an indication that the acid actually does assert a dissociative action on water; that the conductivity of stronger solutions of acid in water are quite small may be due to the great viscosity of the acid solvent. It would be premature, however, to enter more at length into discussions of this nature, because of the fewness of the data and because the work of Kahlenberg and Lincoln<sup>4</sup> shows that not so very much reliance can be placed on the views of Nernst and Brühl.

<sup>1</sup> *Ztschr. phys. Chem.*, 13, 3 (1894).

<sup>2</sup> *Ibid.*, 18, 514 (1895) and 27, 317 (1898).

<sup>3</sup> *Pogg. Ann.*, 159, 233 (1876).

<sup>4</sup> *J. Phys. Chem.*, 3, 12 and 457 (1899).

## ON HUBL'S IODINE METHOD FOR OIL ANALYSIS.

BY AUGUSTUS H. GILL AND WALTER O. ADAMS.

Received November 29, 1899.

THIS method, as is well known, depends upon the fact that the unsaturated glycerides in the oils form addition products with iodine: it has the disadvantage that substitution products—the amount varying with the time of action and strength of the solution—are formed as well. If their formation could be prevented the test would be much increased in value and it was to ascertain if this were possible that this investigation was undertaken.

As ordinarily prepared, the solution contains mercuric chloride and iodine in alcohol: by their interaction mercuric chloriodide and iodine chloride are formed<sup>1</sup> and it is supposed that the latter is the active agent.

$\text{HgCl}_2 + \text{I}_2 = \text{HgClI} + \text{ICl}$ . Ephraim<sup>1</sup> and also Wijs<sup>2</sup> have shown that practically the usual iodine numbers are obtained when a solution of iodine chloride in alcohol is employed. Schweitzer and Lungwitz<sup>3</sup> found that mercuric bromide caused a larger iodine number than the chloride: "that manganese bromide, cadmium, nickel and cobalt chlorides cause practically no addition<sup>4</sup> and that the latter gives the highest true iodine addition figure." As with mercuric chloride, there is no reason why mercuric bromide might not similarly form iodine bromide and this be the active agent.

These metallic salts may play another part in the reaction besides the formation of iodine chloride, that of carriers of halogen, similar to that played by mercury in the Kjeldahl process when dissolving the substance in sulphuric acid. That some such agent is necessary, is shown by the results of Gantter,<sup>5</sup> who found that a solution of iodine in carbon tetrachloride acts very slowly upon the oil and that the results are irregular,—a result which the authors can substantiate, both with oils and oleic acid.

The substance selected as a carrier in the following experiments

<sup>1</sup> *Ztschr. angew. Chem.*, 284 (1895).

<sup>2</sup> *Ber. d. chem. Ges.*, 31, 750.

<sup>3</sup> *J. Soc. Chem. Ind.*, 14, 1031.

<sup>4</sup> It would seem as if this should be "substitution."—Author.

<sup>5</sup> *Ztschr. anal. Chem.*, 32, 181.

was mercuric iodide, and as it is more soluble in methyl than ethyl alcohol the former was employed : that used was free from acetone and anhydrous, being distilled from quicklime. Thirty grams of mercuric iodide and 25 grams of sublimed iodine were dissolved in a liter of methyl alcohol; of this solution 30 cc. were employed for each test and the customary procedure followed. Oleic acid and various oils were used to test the efficacy of this solution ; the oleic acid was the purest obtainable, and gave no test for stearic acid.

The results are given in the accompanying table :

AMOUNT OF IODINE ABSORBED BY VARIOUS ACIDS AND OILS.

A. Acids.

Substance.	Time. Hrs.	Hübl.		Iodide.
Stearic Acid.	4	8.99		7.25
		8.70		6.97
		8.82		6.93
		—		—
Average.		8.84		7.05
Oleic Acid.	4	101.0	91.31	89.19
		100.9	89.64	89.39
		103.5	90.93	90.54
		—	—	—
Average.		101.7	90.2	
	3	—	89.10	89.23
	20	99.38 <sup>1</sup>		97.88 <sup>1</sup>
		98.41		97.50
		98.37		97.65
	25	—		98.02
				97.70
				97.88

B. Oils.

Substance.	Time. Hrs.	Hübl.		Iodide.	
Olive.	4	82	78.9	79.0	79.3
Cottonseed.	4	107	91.6	91.2	92.9
Prime lard.	4	74	72.4	71.6	71.5
Neatsfoot.	4	59	55.8	56.0	55.6

It will be noticed in the case of stearic acid, which should have no iodine absorption, that the substitution, while not

<sup>1</sup> As is evident, considerable substitution has taken place here : this when corrected for gave the theoretical value, 90. This is at variance with the observation of Schweitzer and Lungwitz, *loc. cit.*, 1034.

entirely avoided, is materially lessened by about 20 per cent. With oleic acid, the numbers obtained by the iodide process average but 0.2 per cent. higher than the theoretical, 90 per cent., which is the closest agreement, so far as known, obtained by any process; they are 11 points lower than those obtained by the usual Hübl process. A slight substitution did occur as shown by the hydriodic acid liberated. This was increased by lengthening the time of action of the solution, as seen from the 20- and 25-hour tests; the 3-hour test was conducted to determine if the substitution could not be eliminated by a shorter time. It was found that it did take place, indicating apparently that substitution and addition occur simultaneously: a small amount of substitution was found in the case of the oils as well as with oleic acid.

Attention was called in the early part of this paper to the fact that alcoholic solutions of iodine caused a low and variable addition of halogen to oleic acid; this is more particularly the case if carbon tetrachloride be used as a solvent; chloroform seems to increase this addition very materially. With the former, 66.74, 67.32, and 65.46 per cent. of iodine were added to oleic acid, whereas with the latter, 89.02, 83.66, and 85.86 per cent. were added.

As the solution used contained no halogen but iodine, thus excluding the formation of halides of iodine, and no water, excluding the liberation of oxygen, it would seem that we had here a method which, while as ready of application as the original Hübl, possessed the additional advantage of giving the true iodine figure.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
BOSTON, November, 1899.

## THE IODOMETRIC DETERMINATION OF SMALL QUANTITIES OF CARBON MONOXIDE.

BY LEONARD P. KINNICUTT AND GEORGE R. SANFORD.

Received November 2, 1899.

IN a previous paper<sup>1</sup> one of us mentioned that there might be more danger to be apprehended from the continuous breathing of air containing very small amounts of water gas, such as

<sup>1</sup> *Municipal Engineer*, 17, 71.

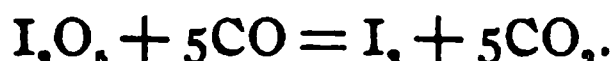


might occur from imperfection in gas fittings than from sewer gas or arsenical wall papers. It is known that air containing 0.3 per cent. of carbon monoxide causes death, 0.2 per cent. very dangerous symptoms, and that mice quickly show the effect of the gas when the air contains only 0.05 per cent. There is reason to believe that air containing even much smaller quantities when breathed for a number of hours may have an effect on the human organism, and on this account the detection and quantitative determination of very small amounts of carbon monoxide when mixed with large volumes of air is a question of importance.

The methods of detecting and estimating very small amounts of carbon monoxide may be divided into two classes: first, those in which carbon monoxyhemoglobin is formed; second, those in which it is oxidized to carbon dioxide. Those of the first class are of little value except for the detection of the gas and they may all be considered as modifications of Hoppe-Seyler's method, first published in 1864,<sup>1</sup> which is based on the fact that while both carbon monoxyhemoglobin, formed by the action of carbon monoxide on arterial blood, and oxyhemoglobin, give two absorption bands in the spectrum; oxyhemoglobin is alone reduced to hemoglobin by the action of such reducing agents as ferrous sulphate or ammonium sulphide.

The method of determining carbon monoxide by oxidation to carbon dioxide has not, until the past few years, received much attention. This oxidation can be accomplished by the use of many oxidizing agents, but of all of those which have been proposed iodine pentoxide is, from our experience, the one that can best be used for the determination of small amounts of carbon monoxide.

Ditte,<sup>2</sup> in 1870, showed that at temperatures between 150°–200° iodine pentoxide was decomposed by carbon monoxide, iodine and carbon dioxide being formed.



This reaction was seemingly first used by C. de la Harpe and F. Reverdine<sup>3</sup> for the detection of the gas, and Nicloux<sup>4</sup> and

<sup>1</sup> *Ztschr. anal. Chem.*, 3, 439 (1864).

<sup>2</sup> *Bull. Soc. Chim.*, 13, 318 (1870).

<sup>3</sup> *Chem. Ztg.*, 12, 1726 (1888).

<sup>4</sup> *Compt. rend.*, 126, 746.

Gautier<sup>1</sup> have made use of the reaction for its quantitative determination.

Nicloux determined the iodine set free, by the depth of color formed in a chloroform solution, and Gautier by the amount of carbon dioxide formed. We have not, by either of these methods, been able to obtain accurate determinations of small amounts of carbon monoxide, but have obtained most satisfactory results by determining the amount of iodine set free, with an N/1000 solution of sodium thiosulphate.

The apparatus used was, with slight changes, that described by Nicloux. Twenty-five grams of iodine pentoxide were placed in a small U-tube, which was suspended in an oil-bath and connected with a Wolff blood absorption tube containing 0.5 gram potassium iodide dissolved in 5 cc. water. The tube containing the iodine pentoxide was also connected with two U-tubes, one containing sulphuric acid, the other small pieces of potassium hydroxide, so as to remove from the air to be analyzed before it came in contact with the iodine pentoxide all unsaturated hydrocarbons, hydrogen sulphide, sulphur dioxide, and similar reducing gases. In all the experiments the oil-bath in which the U-tube containing the iodine pentoxide was suspended, was heated to 150° C., as preliminary tests showed that the reaction was not a quantitative one at lower temperatures.

The iodine pentoxide was made by the action of nitric acid on resublimed iodine, and after this substance had been purified by the usual methods the last traces of free iodine were removed by passing air, freed from all reducing substances, through the iodine pentoxide contained in a U-tube heated to 150° C.

In the experiments which were made to determine the accuracy of the above process, 1 liter of air was usually taken, but as seen in the following tables amounts as small as 250 cc. were tried in several cases and the rate at which the air was passed through the tubes was about 1 liter in two hours, the rate being controlled by forcing the air out of the bottle in which it was contained by dry redistilled mercury, the flow of which was regulated by a glass stop-cock. The amount of carbon monoxide added to the air was accurately measured from a tube made of capillary glass tubing and accurately calibrated so that each

<sup>1</sup> *Compt. rend.*, 126, 931.

division represented 0.005 cc., and readings of 0.001 cc. could easily be made. The temperature and barometric pressure were carefully noted and all volumes were reduced to 0° C. and 760 mm. pressure, and the determination of the iodine set free was made in the Wolff blood absorption apparatus which contained the potassium iodide solution.

With this apparatus, used as described, we were able to determine as small an amount as 0.025 cc. of carbon monoxide, when contained in 1000 cc. of air, or 0.0025 per cent. by volume. The following table gives the results obtained :

ANALYTICAL RESULTS.

Volumes taken.		Iodine liberated.		Difference.
Air.	Carbon. monoxide.	Theoretical.	Found.	
cc.	cc.	Mg.	Mg.	Mg.
1000	0.410	0.941	0.907	0.034
1000	0.286	0.6575	0.6375	0.020
1000	0.359	0.8178	0.7832	0.0346
1000	0.170	0.3859	0.4540	0.0081
1000	0.211	0.4809	0.4775	0.0034
1000	0.151	0.3442	0.3252	0.019
1000	0.115	0.2639	0.2758	0.012
1000	0.061	0.1391	0.1431	0.004
1000	0.023	0.0535	0.0494	0.0041
1000	0.029	0.0672	0.0689	0.0017
1000	0.023	0.0535	0.0495	0.004
500	0.131	0.2993	0.2976	0.0017
250	0.030	0.06862	0.07165	0.0029
250	0.026	0.05967	0.05855	0.0011

Volumes taken.		Carbon monoxide.		Difference.
Air.	Carbon monoxide	Calculated. Per cent. By volume.	Found. Per cent. By volume.	
cc.	cc.			
1000 .	0.410	0.041	0.0395	0.0015—
1000	0.286	0.0286	0.0278	0.0008—
1000	0.359	0.0359	0.0341	0.0018—
1000	0.170	0.0170	0.0197	0.0027+
1000	0.211	0.0211	0.0208	0.0003—
1000	0.151	0.0151	0.0142	0.0009—
1000	0.115	0.0115	0.0119	0.0004+
1000	0.061	0.0061	0.0062	0.0001+
1000	0.023	0.0023	0.0021	0.0002—
1000	0.029	0.0029	0.0030	0.0001+
1000	0.023	0.0023	0.0022	0.0001—
500	0.131	0.0262	0.0260	0.0002—
250	0.030	0.0120	0.0124	0.0004+
250	0.026	0.0104	0.0100	0.0004—

These results showed that by the above method accurate determinations could be made of very small amounts of carbon monoxide in pure air, and it only remained to be proved that the accuracy of the process was not affected when the carbon monoxide was mixed with air containing illuminating gas, and experiments were made to determine the action of hydrogen, marsh-gas, unsaturated hydrocarbons, hydrogen sulphide, and sulphur dioxide on iodine pentoxide.

Hydrogen and marsh-gas, as was to be expected, had no effect on the iodine oxide at  $150^{\circ}\text{C}$ . and the unsaturated hydrocarbons, hydrogen sulphide and sulphur dioxide, in much larger amounts than are contained in illuminating gas, or formed by its combustion, were perfectly absorbed, when passed in the way described through U-tubes containing sulphuric acid and potassium hydroxide.

These facts having been determined, mixtures of illuminating gas and air were made, and the amount of carbon monoxide determined.

The experiments gave the following results :

The gas used contained 18.6 and 19.0 per cent. of carbon monoxide, respectively. Of the first, 0.104 cc. was added to 1 liter of air and the air was found to contain 0.019 cc. carbon monoxide, the calculated amount being 0.0191 cc. In the second case, 0.146 cc. of the gas was taken and the air gas found to contain 0.027 cc. of carbon monoxide in place of 0.02789 cc.

The results that have thus been obtained show that the presence and amount of carbon monoxide in the air of a room can be determined when the air contains above 0.0025 per cent. by volume, or 2.5 volumes in 100,000 volumes of air, and if the presence of this gas is due to leakage of illuminating gas and the per cent. of carbon monoxide in this gas is known, the amount of illuminating gas contained in the air can, of course, approximately be calculated.

## THE TECHNICAL ANALYSIS OF LICORICE PASTES.

BY M. TRUBEK.

Received November 14, 1899.

WHEN I was first confronted with the analysis of licorice products, I had to select a method, which, giving the necessary data required by the trade, could easily be carried out in a reasonably short time.

The literature on that subject was found to be rather meager and only fragments could be found here and there. More comprehensive was the article on the subject of licorice found in Hager's *Pharmaceutische Praxis*, and for the determination of some constituents the method therein described was at first carried out with a few minor modifications; instead of taking 10 grams of substance as prescribed only 2 grams were used. The first amount required too large quantities of ammonia and alcohol on one hand and absolute alcohol on the other hand to get a colorless filtrate, besides requiring too much time, extra large filters and weighing-bottles. It soon developed, however, that the above method gave too high results in glycyrrhizin, which results were out of question, in case glucose had been added to the paste, as the following figures will show:

	Glycyrrhizin. Per cent.
1. Paste with no glucose added .....	22.25
2. Same paste with 15 per cent. glucose added.....	29.61
3. " " " 20 " " " " .....	34.12

Instead of going down on glycyrrhizin as it should be through the addition of the glucose, the values for that substance rose with the amount of glucose added. It was examined for that substance as glucose might have been thrown down together with the glycyrrhizin and was not entirely removed during washing, by precipitating the glycyrrhizin with basic lead acetate but only about 2 per cent. of glucose were found in No. 2, not explaining the rise in glycyrrhizin. I concluded therefore that that rise was due to the presence of a substance or substances formed from the glucose by the ammonia, especially while concentrating the run-off from the first operation, which substances were absolutely insoluble in absolute alcohol and could not be washed out by the same. After several experiments along those lines the following mode of operation was adopted and found to work satisfactorily.

To 2 grams of the extract to be examined add 5 cc. water, place on a warm plate, and by means of a glass rod make up to a perfectly even mass. Add little by little, while stirring, 20 cc. of 96 per cent. alcohol and allow to settle. Filter through a weighed filter and wash with a mixture of 1 part water and 4 parts alcohol of above strength until run-off is colorless, which takes about 100 cc. of wash liquor. Keep the top of the filter wet, as it easily dries out and is then washed with difficulty. The filter, with contents, is dried at 105° C. for three hours and weighed. It gives the gummy matter, starch, etc., contained in the extract. The filtrate is either distilled off or evaporated. Take a large beaker for evaporating, or else liquor creeps up to the edges incurring losses. When nearly evaporated transfer to a small beaker, evaporate further to a thick sirup, making about 1 or 1.5 cc. It is then dissolved in 2 cc. glacial acetic acid, and 30 cc. absolute alcohol are added with constant stirring. Too violent stirring produces a lumpy mass, which is difficult to wash out. The solution is allowed to settle. Filter through a weighed filter, wash with absolute alcohol until no acid reaction, dry at 105° C. for three hours, and weigh. The figure obtained is not pure glycyrrhic acid, but rather a salt. To get the acid sufficiently accurate, an aliquot part is incinerated, using blast heat at the end, and deducting 0.7 of the percentage of ash from the percentage of the salt found. The ash consists mainly of calcium oxide, but contains also very small amounts of alumina and magnesia.

The glycyrrhizin salt as prepared by my method represents a light yellow amorphous powder, soluble in glacial acetic acid, cold and hot water, and dilute alcohol. It has a very sweet taste. (The pure glycyrrhic acid is according to Haberman<sup>1</sup> a tribasic acid and forms acid and normal salts. It dissolves in the same reagents as the salt above described, but only in hot water, while making a jelly with cold water.)

The filtrate from the glycyrrhizin is distilled off, diluted and evaporated, and this repeated until the acetic acid is driven off. The residue is dried at 105° C. for three hours and weighed. This amount represents the so-called extractive matters, containing the saccharine matter that the root contained originally or which had been added subsequently to the paste; they contain also some tannin, resin, etc.

<sup>1</sup> *Ann. Chem.* (Liebig), 197, 105.

Ash, in the paste, is determined by incinerating 2 grams in a platinum dish. For total solids, about 5 grams are dissolved in hot water and made up to 500 cc. after cooling the liquor. It is well shaken and 50 cc. are evaporated, dried at 105° C. for three hours, and weighed.

For solids soluble in cold water, 50 cc. of the clear filtrate are evaporated, dried, and weighed. For evaporation, flat bottomed, so-called crystallizing glasses have been found to be very convenient.

The difference between "total solids" and "soluble solids" represents the residue insoluble in cold water.

The moisture is taken as the amount obtained by subtracting the "total solids" from 100.

Reducing substances are determined as usual after precipitating with basic lead acetate and titrating the filtrate, freed from lead, with standardized Fehling's solution.

Following are the results obtained by the above method from different samples of licorice extract :

	1. Per cent.	2. Per cent.	3. Per cent.	4. Per cent.
Moisture .....	24.18	25.14	19.58	23.99
Residue insoluble in cold water.	3.95	6.79	14.35	2.54
"      "      " mixture of				
1 water and 4 alcohol.....	27.27	25.20	36.58	24.65
Glycyrrhizin .....	22.78	21.97	18.51	19.90
Extractive matter .....	25.02	25.05	26.02	28.91
Ash .....	6.25	6.02	5.60	5.59
Reducing matters as glucose....	....	....	....	9.76

Sample No. 1 was one of Scudder's brands.

Sample No. 4 gave, by the method described in Hager's *Pharmaceutische Praxis* for glycyrrhizin, 28.57 per cent.

An analysis of fresh and spent licorice root gave the following results :

	Fresh. Per cent.	Spent. Per cent.
Moisture .....	8.40	10.00
Total solids.....	33.18	10.86
Cold solubles .....	29.65	....
Gummy matter, starch, etc .....	8.07	3.56
Glycyrrhizin .....	11.21	2.25
Extractive matters.....	14.77	5.60
Ash .....	2.68	0.55
Reducing matters.....	0.52	....

# BENZENESTEARSULPHONIC ACID AND OTHER SULPHONIC ACIDS CONTAINING THE STEARIC RADICAL.<sup>1</sup>

BY E. TWITCHELL.

Received November 29, 1899.

IN connection with some experiments on the action of sulphuric acid on the higher fatty acids I prepared a mixture of benzene and oleic acid and treated this with an excess of concentrated sulphuric acid. I found that a union took place between the benzene and the oleic acid, and at the same time a sulphonic acid was formed.



To prepare this benzenestearosulphonic acid, a mixture of oleic acid and benzene is treated with a large excess of concentrated sulphuric acid, avoiding any excessive rise in temperature by cooling the mixture and by adding the acid slowly. After several hours the greater part of the oleic acid will have combined as expressed by the above equation, and the benzenestearosulphonic acid can be separated and freed from the excess of the original components of the mixture and from the results of secondary reactions which have occurred.

A consideration of the action of sulphuric acid on oleic acid will make it plain that these impurities can only be the following :

1. Unacted-on oleic acid ;
2. Other fatty matters, such as oxystearic acid and fatty anhydrides, produced by the action of the sulphuric acid and subsequent decomposition of the sulpho compounds ;
3. Unacted-on benzene ;
4. Stearosulphuric acid,  $\text{C}_{18}\text{H}_{33}\text{O}_2\cdot\text{HSO}_4$  ;
5. Benzenesulphonic acid ;
6. Sulphuric acid in large excess.

From its mixture with these substances the pure benzenestearosulphonic acid can be separated by virtue of the following properties it possesses, to which I will again refer: It is soluble

<sup>1</sup> Read before the meeting of the Cincinnati Section, November 15, 1899.



in water, but can be rendered completely insoluble (salted out) by the presence in the water of a little hydrochloric acid or sulphuric acid. It is very stable, not decomposed by boiling with acid solutions. It is insoluble in petroleum ether.

The reaction mixture is treated with water and heated to boiling, whereby the excess of sulphuric acid is diluted and the mass separates into two layers; the lower, a clear aqueous liquid, contains the excess of sulphuric acid and whatever benzenesulphonic acid may have been produced. The upper layer, a viscous oil, contains the benzenestearosulphonic acid with the remaining impurities insoluble in dilute sulphuric acid. If any stearosulphuric acid was present, this will have been decomposed by the heating into sulphuric acid and oxystearic acid and anhydrides. The lower layer is removed and the upper is washed with water containing hydrochloric acid until free from sulphuric acid. By this operation the benzenesulphonic acid is also washed out. The oily layer is now washed a number of times with petroleum ether, which dissolves the oleic acid, the benzene, and the other fatty matters before mentioned, leaving the compound pure except for small quantities of water and hydrochloric acid, and these can easily be removed by drying at 100° C.

The washing with petroleum ether is a tedious process, as some of the decomposition products of oleic acid are rather difficultly soluble in this liquid. For this reason, when quantitative results are not required, it is better to dissolve the partially purified product in ether and shake with water. The aqueous extract, containing most of the benzenestearosulphonic acid, is treated with a little hydrochloric acid, taken up with ether and again extracted with water. On evaporating the aqueous solution the compound is obtained in a pure state.

The composition of the compound was determined by the estimation of the sulphur and carbon and by its acid equivalent, it being a dibasic acid containing an acid hydrogen of the sulphonic radical, which can be exactly titrated by using methyl orange as indicator, and an acid hydrogen of the fatty radical which can be titrated with phenolphthalein as indicator.

The several analyses represent samples prepared at different times.

	Sulphur.	Carbon.	Ratio of sulphur to carbon.	$\pi/10$ alkali re- quired to com- bine with $\text{SO}_3$ H group in 1 gram of sub- stance. Methyl orange as indicator. cc.	Additional $\pi/10$ alkali re- quired to com- bine with the fatty group. Phenol- phthalein as indicator. cc.
Calculated for $\text{C}_{10}\text{H}_8.\text{SO}_3\text{H}.\text{C}_{18}\text{H}_{35}\text{O}_2$ .	7.2727	65.45	9.00	22.727	22.727
Found 1				21.56	22.41
" 2	7.12			22.49	22.44
" 3	7.22	64.70	8.96	22.66	23.19

The composition was further fixed by the determination of the weight of benzenestearosulphonic acid obtained from the oleic acid which entered into the reaction. From the molecular weights of the two compounds, 282 parts of oleic acid would yield 440 parts of benzenestearosulphonic acid, or the yield on 100 parts of oleic acid would be 156.03.

An accurately weighed, quantity of oleic acid was mixed with benzene and then treated with an excess of sulphuric acid. After removing the impurities soluble in acidified water, the product was extracted with petroleum ether, the extract weighed and deducted from the amount of oleic acid taken. The difference was that which had combined with benzene and sulphuric acid. The residue insoluble in petroleum ether was also dried and weighed, giving the yield of benzenestearosulphonic acid.

In two experiments 100 parts of oleic acid were found to yield 151.0 and 156.7 parts of benzenestearosulphonic acid.

In this calculation there is an error, in that the petroleum extract does not consist wholly of unaltered oleic acid, but also contains oxystearic acid and anhydrides; but this error is very small considering the small quantity of oleic acid deducted as a correction, and the fact, established by an experiment, that the weight of the fatty matter is only slightly altered on treating oleic acid alone with sulphuric acid and then decomposing by boiling with water.

Benzenestearosulphonic acid resembles in its physical characteristics, and also in many of its chemical ones, the stearosulphuric acid obtained by acting on oleic acid in the cold with concentrated sulphuric acid. At  $100^\circ\text{C}$ . the dry compound is a very viscous oil, while at ordinary temperatures it is a sticky, semisolid mass. It, as well as its mono- and di-alkaline salts,

is soluble in water in all proportions, yielding colloidal solutions which, on agitating, form a strong lather and are precipitated (salted out) by any strong acid, base or salt. The free acid is perfectly stable in boiling water, even in the presence of mineral acids, differing in this from stearosulphuric acid. On heating to high temperatures with hydrochloric acid it decomposes only very slowly. A small quantity heated in a sealed tube to  $170^{\circ}\text{C}$ . for three and a half hours, had decomposed only to the extent of 15 per cent.

Benzenestearosulphonic acid when fused with caustic potash gives potassium sulphite. Here again it differs from stearosulphuric acid, which when similarly treated yields potassium sulphate.

As shown by the formula, benzenestearosulphonic acid is dibasic, the two acid hydrogens having very different strengths, so that, as has been already pointed out, they can be independently titrated with caustic soda solution, using different indicators.

## NAPHTHALENESTEARSULPHONIC ACID,



This compound is prepared and purified in a manner precisely similar to that used in the preparation of the benzene compound, which it closely resembles, being, however, rather less fluid in its character.

The analysis gives the following results :

		$n/10$ alkali required to combine with the $\text{SO}_3\text{H}$ group in one gram of substance. Methyl orange as indicator.	Additional $n/10$ alkali required to combine with the fatty group in 1 gram of substance. Phenolphthalein as indicator.
		cc.	cc.
Calculated for $\text{C}_{10}\text{H}_6.\text{SO}_3\text{H}.\text{C}_{18}\text{H}_{35}\text{O}_2$		20.408	20.408
Found	1	20.07	19.97
"	2	20.28	20.17
"	3	20.35	20.41

## PHENOLSTEARSULPHONIC ACID,



This compound is prepared like the others and closely

resembles them in its character. The following analytical results show that the compound had not been obtained pure.

	$\pi/10$ alkali required to combine with the $\text{SO}_3\text{H}$ group in 1 gram of substance. Methyl orange as in- dicator.	Additional $\pi/10$ alkali required to combine with the fatty group in 1 gram of substance. Phenolphthalein as in- dicator.
	cc.	cc.
Calculated for $\text{C}_6\text{H}_5\text{OH}.\text{SO}_3\text{H}.\text{C}_{18}\text{H}_{35}\text{O}_2$ .	21.929	21.929
Found 1	24.47	20.39
" 2	29.75	20.77

These results clearly indicate the presence of a disulphonic acid. This I have not yet attempted to separate, but its quantity can be calculated and allowed for, and if this is done it will be seen that the figures will agree closely with those required by the formula.

In much of the analytical work described in this paper and also in the preparation of some of the compounds, I was kindly assisted by Mr. Wm. Simonson.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 12.]

## A NEW INTERRUPTER FOR THE KOHLRAUSCH-OSTWALD CONDUCTIVITY METHOD.

BY J. LIVINGSTON R. MORGAN.

Received December 7, 1899.

IN a recent paper<sup>1</sup> I described three useful additions to the Kohlrausch-Ostwald conductivity method. Since then an improvement has been made in the interrupter, the first of the three described, which simplifies it to such an extent that a description of it is deemed advisable. In the apparatus as first proposed, the primary current (2-5 volts from the electric light circuit or from storage cells) was used to charge the vibrating wire as well as to excite the electromagnet. The current from the cell used in the conductivity apparatus was then connected, through the vibrating wire and an extra mercury cup, to a small induction coil (without the breaker), the secondary of the coil being connected to the bridge arrangement in the usual way. The intermittent current produced by the vibrating wire and the mercury cup becomes a rapidly alternating one, such as is desired, in passing through the induction coil.

<sup>1</sup> This Journal, 22, 1 (1900).

In the new form, one of the mercury cups is dispensed with entirely, and the current from the cell of the conductivity apparatus alone goes through the wire causing it to vibrate, and thus with the mercury cup to make and break the circuit. In the Pupin arrangement<sup>1</sup> using the permanent magnet, one cell is

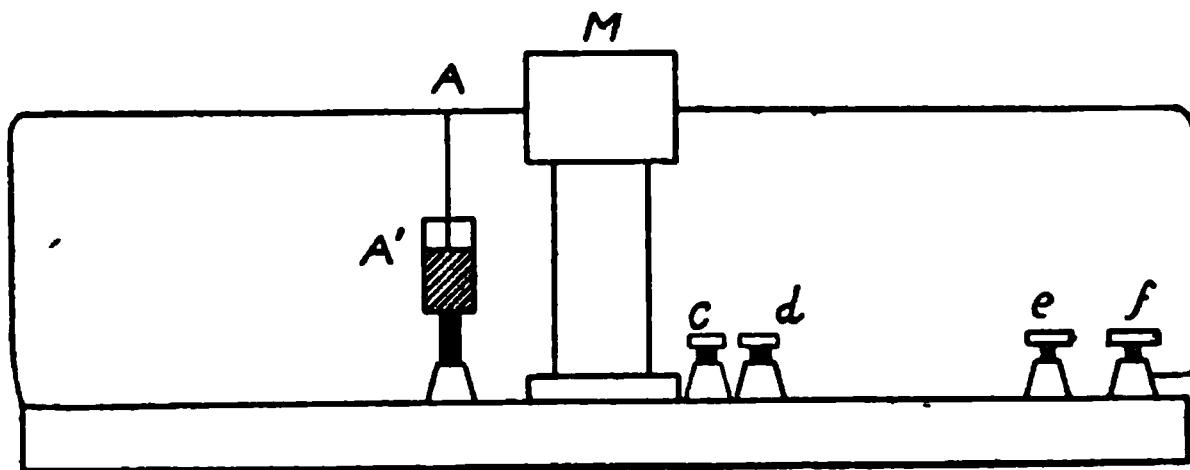


Fig. 1.—*c* and *d*, the binding posts of the electromagnet, are connected to the electric light circuit (3 to 5 volts). *c* is connected under the base to the mercury cup *A'*.

insufficient to cause a vibration but by the use of an electromagnet the strength of the magnetic field can be so intensified that the wire is repelled even when carrying a very small current. Fig. 1 shows the arrangement of the new form of

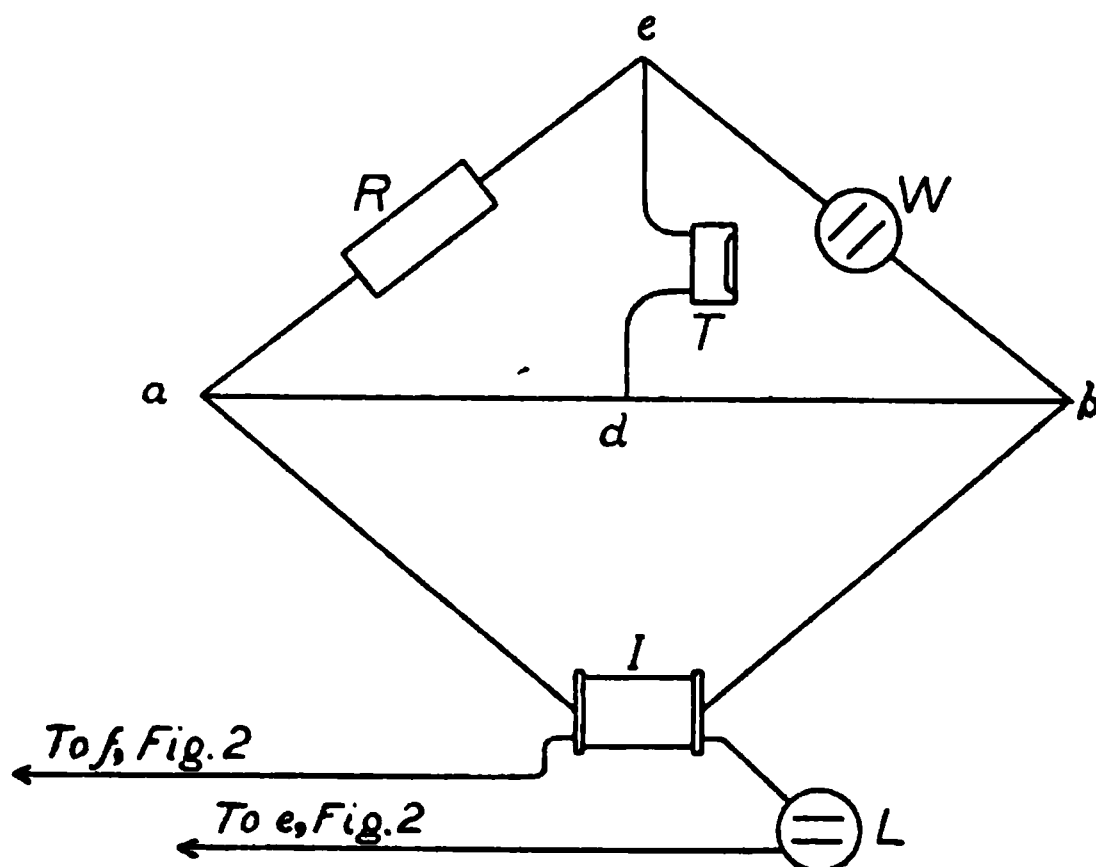


Fig. 2.—*R* is the known resistance, *W* the electrolytic cell, *I* the coil, *L* the Lelanché cell and *T* the telephone. The current breaker of the coil *I* is removed.

apparatus. The electromagnet is excited by a current of from 2 to 5 volts entering at the posts *c* and *d*. The current from the battery *L* (Fig. 2) is connected to the primary of the induction coil *I* through the posts *e* and *f* (Fig. 1). The dipper of the

<sup>1</sup> *Am. J. Sci.* [3], 45, 325 (1893).

wire  $A$  is in contact with mercury  $A'$  in the adjustable cup, which is connected by a wire under the base to the post  $e$ . The current then goes from one pole of the battery  $L$  to  $f$ ,  $A$ ,  $A'$ ,  $e$  and then through the primary of the induction coil back to the other pole. When the current is passing through the wire the magnet will repel the wire, and if the cup  $A'$  is at the proper height the contact with the mercury will be broken and since the wire when uncharged is not affected by the magnet its tension will make the contact once again and the same process will be repeated. The tension of the wire and consequently the rapidity of vibration, may be altered by the screw devices at each end.

This new form of apparatus is not only simpler in construction than the original, but is also much more readily adjusted and kept in adjustment. In the earlier form with two mercury cups it is necessary that the wire vibrate in such a way that loops are formed at the two cups, so that the original adjustment is more difficult to make and a variation in the number of vibrations per second is less easy to arrange. If three or more pieces of conductivity apparatus, each with its cell, are connected to the same vibrator, a smaller voltage may be used for the electromagnet, for the voltage in the wire is much greater and consequently the strength of the magnetic field may be much reduced and still give the same result.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 13.]

## THE SPECIFIC GRAVITY AND ELECTRICAL RESISTANCE OF METALLIC TELLURIUM.

BY VICTOR LENHER AND J. LIVINGSTON R. MORGAN.

Received January 2, 1900.

IN this Journal<sup>1</sup> one of us described the preparation of metallic tellurium by means of the reduction of an alkaline solution of the oxide of tellurium with sugar. A description was given in that paper of the means used to test the tellurium for impurities. The tellurium obtained by reducing with sugar was found to be volatile in hydrogen gas leaving no residue. Its oxide was found to be completely volatile in hydrochloric acid gas.

<sup>1</sup> Lenher: This Journal, 21, 348.

As a further means of establishing the purity of the metal, a few physical tests were made. The specific gravity was carefully determined and a great deal of time was spent in attempting to determine its electrical resistance.

*Determination of the Specific Gravity.*—For this purpose, material was selected, which had been twice distilled in hydrogen.

The metal was finely powdered, as a number of preliminary experiments showed that owing to the great crystalline tendency that the metal exhibits, it is almost impossible to obtain a specimen of any size which does not contain gas. Consequently, it was found that reasonably constant results could be obtained only when the metal was carefully broken up.

The experiments were carried out in an ordinary 15 cc. pycnometer, pure water being used as the medium. The temperature was 20°. In order to expel the adhering air bubbles, the water with the metal was heated and the vessel allowed to stand over night to cool.

	Weight tellurium taken.	Sp. gr.
Experiment 1....	11.9727	6.194
“ 2	11.9146	6.200
“ 3	16.0946	6.204
Mean		6.1993

This figure is a trifle less than that obtained by Spring<sup>1</sup> but is almost identical with that obtained by Klein and Morel<sup>2</sup>. The latter chemists obtained the figures 6.204 and 6.215, while Spring obtained a figure slightly higher, 6.22.

The latest figure previous to our work is by Priwoznik<sup>3</sup> who obtained 6.2459 at 18.2°.

*Determination of the Electrical Resistance.*—For the determination of the electrical resistance of a metal, it is advisable to obtain great length and small diameter of the substance. With tellurium this is almost impossible. The metal is extremely crystalline, more strongly so than any metal which has come into our hands. As a result of this tendency, the metal, when of small diameter and possessing any appreciable length, is so weak that a rod grasped by the end will snap off, it not being able to sustain its own weight.

<sup>1</sup> *Bull. Acad. Roy. Belg.* [3], 2, 88-110 (1881).

<sup>2</sup> *Ann. Chem.* (Liebig), [6], 5, 61

<sup>3</sup> *Chem. Centrbl.*, 2, 962 (1892).

It is not practical to cast the metal in cold moulds. Various attempts were tried in this direction but proved unsuccessful. The best method for obtaining a suitable section was found to be to melt the metal in a thin glass tube of comparatively narrow bore. To this end an open glass tube was placed in an inclined combustion furnace and inside of it was introduced a smaller tube closed at one end and containing the metal to be fused. The fusion took place at a low red heat, while in the liquid condition, the tube was gently tapped until all of the gas escaped.

Slow cooling tends to produce larger crystals and the metal is correspondingly more brittle. Rapid cooling, on the other hand, gives smaller crystals, but the difference in resistance is not apparent. The most satisfactory results were obtained by jacketing the tube of molten tellurium with a larger tube also containing fused metal. Although in this instance the metal cooled under the pressure of the shell in the jacket, the only apparent difference was that longer sticks could be obtained.

From the many fusions that have been made in this laboratory, it appears that tellurium on cooling, first contracts until it solidifies, then slightly expands. As an example of this may be noted that each stick contained a depression in its upper part, which extended about one-fifth of the entire length<sup>1</sup> and that the tubes always cracked just after the metal solidified. The tubes invariably cracked at this time, no matter how carefully they had been annealed, nor how slowly they were cooled.

In order to obtain the best possible contact, a piece of rubber tubing was drawn over each end of the stick to be measured and the tubes filled with mercury. The latter was connected with a small dry battery, a wheatstone bridge and galvanometer being in the circuit.

*No. 1.*—Length, 100 mm., diameter, 7.42 mm. Resistance at 20° = 1.38 legal ohms. Specific resistance = 596.6.

*No. 2.*—Length 162 mm., diameter, 8.89 mm. Resistance at 20° = 1.23 legal ohms. Specific resistance = 463.6.

*No. 3.*—Length, 137 mm., diameter, 8.255 mm. Resistance at 20° = 1.46 legal ohms. Specific resistance = 569.9.

*No. 4.*—Length, 103 mm., diameter, 3.43 mm. Resistance at 20° = 3.68 legal ohms. Specific resistance = 330.1.

<sup>1</sup> This portion was always removed before measurements were made.



*No. 5.*—Length, 82 mm., diameter, 3.43 mm. Resistance at  $20^{\circ} = 2.48$  legal ohms. Specific resistance  $= 279.4$ .

This specimen was a piece of No. 4 after a portion had been broken off.

*No. 6.*—Length, 84.5 mm., diameter, 3.05 mm. Resistance at  $20^{\circ} = 5.88$  legal ohms. Specific resistance  $= 508.3$ .

*No. 7.*—Length, 86.1 mm., diameter, 4.83 mm. Resistance at  $20^{\circ} = 5.37$  legal ohms. Specific resistance  $= 1152$ .

On close examination this bar was found to be cracked.

*No. 8.*—Length, 57.5 mm., diameter, 2.92. Resistance at  $20^{\circ} = 4.68$  legal ohms. Specific resistance  $= 544.5$ .

As all of the bars showed a strong cleavage on the ends, the measurements could only be approximate, and when they are calculated to the standard conditions, one meter in length, with a cross section of one mm., the errors of measurement are correspondingly multiplied.

By using an ordinary copper clamp contact, almost any resistance can be obtained according to the amount of pressure exerted by the clamp; no difference in resistance could be detected when working in the light or dark.

By comparison of the results obtained, it will be observed that the mean would be about 500; however, from the great tendency to crystallization that the metal shows, it would seem more probable that the lowest result more nearly approaches the true figure. As gas carbon has a specific resistance equal to 50, the resistance of tellurium is seen to be enormous. The result obtained by Matthieson,<sup>1</sup> 0.000777 for the conductivity compared with silver as 100, would give a specific resistance of more than 2000, showing that the structure of his metal must have been different from ours or that different contact was made.

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## THE VOLUMETRIC DETERMINATION OF MAGNESIA.

BY JAMES OTIS HANDY.

Received January 2, 1900.

EVERY chemist, who has to make many determinations of magnesia in water, cement or other material, appreciates the difficulties surrounding the gravimetric process. These difficulties chiefly arise from the fact that the change from magne-

<sup>1</sup> *Pogg. Ann.*, 103, 428.

sium ammonium phosphate to the pyrophosphate of magnesia is attended by a rapid consolidation or sintering of the mass. By this means particles of carbon from the filter-paper are often firmly enclosed in the lumps of precipitate.

If gradual heating over a Bunsen burner is continued long enough, fifteen minutes over the blast-lamp with crucible inclined and cover placed in a position to facilitate oxidation, will give a pure white pyrophosphate. If, however, the preliminary heating proceeds too rapidly, or is not continued long enough before applying the blast, it is almost impossible to burn off all the carbon.

The method recommended by Fresenius for completing the oxidation of such material by treatment with nitric acid followed by evaporation and re-ignition, yields a pure white residue, but the result is invariably low. The author found that pure magnesium pyrophosphate when so treated lost weight every time, although no mechanical loss took place. Moreover, repetition of the treatment caused further serious loss. Constant weight was not reached.

No one who has adopted the volumetric method for determining calcium oxalate by means of standard permanganate would ever go back to the gravimetric way. When a simple and accurate method for the volumetric determination of magnesia appears, it will be equally useful.

The alkalimetric method published by Stolba in 1866<sup>1</sup>, referred to by Sutton, Hart, Meade<sup>2</sup> and others, has not come into general use. The reaction is:



Its unpopularity is doubtless due to the use of alcohol for removing the ammonia wash from the magnesium ammonium phosphate precipitate, it being an expensive and tedious procedure.

Meade proposes a radical change from the usual phosphate method. He estimates the magnesia by precipitating it as arsenate and determines by standard thiosulphate the amount of iodine which a hydrochloric acid solution of the precipitated arsenate liberates from potassium iodide. The procedure seems

<sup>1</sup> *Chem. Centrbl.*, 728 (1866).

<sup>2</sup> *This Journal*, 21, 746 (1899).

rapid and accurate, but it would appeal only to those who prefer an iodometric to an alkalimetric method.

The writer has endeavored to eliminate the objectionable feature of Stolba's method by discarding alcohol and removing the free ammonia from the phosphate precipitate by taking advantage of the volatility of ammonia.

It was necessary to find some way of expelling the ammonia without in any way affecting the integrity of the phosphate which should remain. In view of the fact that Fresenius, Roscoe and Schorlemmer, and other authorities all agree that the only change which  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  suffers at  $100^\circ \text{C.}$ , is the loss of 5 molecules of water of crystallization, it seemed a simple thing to put filter and precipitate into 50 cc. of distilled water, and after removing the ammonia by boiling down to 30 cc., to cool, add a measured excess of standard acid to dissolve the precipitate, and then to titrate back with standard alkali. After many trials in which the results were all low and irregular this method was abandoned. Evidently some change of composition took place at  $100^\circ \text{C.}$  under these conditions.

Other means of subjecting the ammoniacal precipitate to this temperature were tried. The filters containing the precipitates were spread out flat on strong 5-inch filters, and were placed, one set at a time, in a funnel through which a current of steam was rising, and allowed to remain for ten minutes. The ammonia was expelled, but the results by titration were still low, although absolutely no mechanical loss or loss by solution took place. There was a loss in alkalinity due to a chemical change other than the loss of water of crystallization.

Thinking that the presence of water in the one, and of steam in the other of these experiments, might have brought about a change which temperature alone could not have accomplished, a set of experiments were made wherein the filters and precipitates were dried in an oven at  $100^\circ \text{C.}$ , away from all but the moisture which they at first contained. By this means also, low results were obtained.

It was then apparent that no rapid or satisfactory method could be based on titration of magnesium ammonium phosphate which had been dried at  $100^\circ \text{C.}$ , or even heated to that temperature without drying. Although the change in alkalinity

might be perfectly definite and complete, it would require much longer for large precipitates to be completely transformed than for small ones, and irregular results would surely be obtained.

Before rejecting the statement of such eminent authorities with regard to the effect of drying magnesium ammonium phosphate at 100° C., it was thought best to completely eliminate the moisture element from the experiment.

A quantity of the pure salt was prepared by precipitation under standard conditions from a solution of magnesium chloride. After washing thoroughly with 10 per cent. ammonia wash (1 part of ammonium hydroxide, sp. gr. 0.90, mixed with 9 parts of water), the precipitate was spread out on filter-paper and allowed to dry in the air. It was then dried over sulphuric acid, after which it was ground, mixed and placed in a stoppered bottle. Weighed portions were then tested for purity, and this having been established, the property in question was examined into.

PROPERTIES OF  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ .

	Statement of authorities. Per cent.	Actual facts. Per cent.
Loss of weight at 100° C. (water, etc.) .....	36.70	41.43
Yield of $\text{Mg}_2\text{P}_2\text{O}_7$ on ignition.....	45.34	45.59
Cc. $\frac{N}{10}$ $\text{H}_2\text{SO}_4$ for 1 gram before 100° drying ....	82.05	81.94
The same if dried at 100° C. beforehand.....	82.05	54.59
Loss of original alkalinity at 100° C. (per cent.) 00.00		33.38

The author does not wish to be understood as saying that the first column in the above table represents verbatim the statements of Fresenius and others, but that it does represent the exact results which would follow if their statements were true.

By comparing the magnesium oxide value of decinormal sulphuric acid when used on air-dried  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  with the value when a weighed amount of the same salt is heated to constant weight at 100° C. before titration, it will be seen that the difference is very great.

1 cc.  $\frac{N}{10}$   $\text{H}_2\text{SO}_4$  = 0.002 gram MgO in the air-dried salt.

1 cc.  $\frac{N}{10}$   $\text{H}_2\text{SO}_4$  = 0.003 gram MgO in the same material if first dried at 100° C.

Although the definiteness of this change is now firmly established, the formula of the compound which is formed at 100° C., has not yet been determined.

The folly of drying at 100° C. as a preliminary to the titration of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  having been established, the author determined to ascertain the speed with which ammonia evaporated from phosphate precipitates at ordinary temperature. It was found that if filters containing precipitates were opened flat after washing, and placed face upward on heavy dry filter-paper of the sort made by Whitall, Tatum & Co., for druggist's use, the bulk of the moisture would be drawn out in a few minutes, and if transferred then to a second dry paper and allowed to stand for half an hour to one hour, the ammonia, so far as its power of neutralizing a measurable quantity of acid was concerned, had entirely disappeared. When the filter-papers have become dry for a distance equal to one-fifth of the diameter of the paper, measured from the outer rim, it is certain that the ammonia has been expelled. This is, of course, based on the assumption that the precipitate is distributed fairly evenly over the rest of the paper.

Methyl orange was the indicator used, and in all cases a clear yellow was considered the end-point when using decinormal sodium hydroxide to measure the excess of decinormal sulphuric acid.

TITRATION OF  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ .

	Time for precipitation.		Time of drying.		Temperature.	MgO used.	MgO found.	Error.
	Hrs.	Min.	Hrs.	Min.		Gram.	Gram.	Gram.
1	3	0	18	6	21° C	0.00475	0.00478	0.00003
2	3	0	18	6		0.01900	0.01900	0.00000
3	3	0	18	6		0.02375	0.02377	0.00002
4	3	0	18	6		0.04750	0.04785	0.00035
5	1	30	2	0	19	0.02375	0.02377	0.00002
6	1	30	2	30	19	0.02375	0.02377	0.00002
7	1	30	3	0	19	0.02375	0.02377	0.00002
8	1	30	3	20	19	0.02375	0.02377	0.00002
9	1	30	2	0	19	0.02375	0.02377	0.00002
10	1	30	1	0	19	0.02375	0.02377	0.00002
11	1	30	1	0	21	0.04750	0.04775	0.00025
12	1	30	1	30	21	0.01907	0.01990	0.00083
13	1	30	1	30	21	0.01907	0.01930	0.00023
14	1	30			21	0.03814	0.03830	0.00016
15	1	30	1	30	21	0.05720	0.05740	0.00020
16	1	30	1		21	0.05720	0.05780	0.00060
17	1	30		30	21	0.01907	0.01920	0.00013
18	1	30		30	21	0.01907	0.01920	0.00013

	Time for precipitation.		Time of drying.		Tempera- ture.	MgO used. Gram.	MgO found. Gram.	Error. Gram.
	Hrs.	Min.	Hrs.	Min.				
19	1	30	0	45	21	0.03814	0.03830	0.00016
20	1	30	1	15	21	0.03814	0.03800	0.00014
21	1	30	1	0	21	0.05720	0.05670	0.00050
22	1	30	1	0	21	0.05720	0.05680	0.00040
23	1	30	0	25	65	unknown	0.05650	
24	1	30	0	25	65	unknown	0.05650	
25	1	30	1	15	21	unknown	0.05650	
26	1	0	1	0	21	0.04767	0.04711	0.00056
27	1	0	0	20	59	0.04767	0.04771	0.00004
28	1	0	0	40	{ 62 av. 66 max.	0.04767	0.04671	0.00096
29	1	0	1	0	{ 62 av. 66 max.	0.04767	0.04631	0.00136
30	{ 5 shaking 30 standing }			60	21	0.00095	0.00090	0.00005
31	{ 5 shaking 45 standing }			60	21	0.00048	0.00050	0.00002

Experiments like the above prove the accuracy of the alkali-metric method for magnesia determination. The cases of significant error in the table may be divided into those caused by imperfect removal of the ammonia (Nos. 12 and 16); those caused by drying too long and at too high a temperature in the oven (Nos. 28 and 29); those doubtless caused by imperfect manipulation (Nos. 21, 22, and 26); and, finally, those inherent in the process itself. The latter are all very small if, indeed, they exist at all. Experiments 23, 24, and 25 are comparative only.

Experiments Nos. 30 and 31 show not only the extreme delicacy of the reaction on which the method depends, but they show how rapid the reaction is, even in very dilute solutions, and how insoluble the phosphate is in 10 per cent. ammonia wash.

It was found that five minutes' shaking in a stoppered flask at ordinary temperature sufficed, if followed by fifteen minutes' standing, to completely precipitate any magnesia solution containing as much as 0.002 gram of magnesium oxide in 100 cc. With amounts exceeding 0.05 gram per 100 cc., it is believed that filtration could be begun in five minutes after the end of the shaking process.

In order to ascertain what temperature could be safely used to expedite the expulsion of ammonia from the phosphate precipitates, a series of experiments were made. It was found that

at 55° C. there was no appreciable loss of alkalinity but that at 65° a loss of 1 per cent. had taken place. Several experiments in which the filters and precipitates were removed from the oven as soon as the outer half-inch of the papers were dry, gave identical results with air-drying at 21° C. From fifteen to thirty minutes in the oven at 50° to 60° C. suffices. If the drying of the precipitate proceeds too far, solution in decinormal sulphuric acid is slow. If, however, the drying is stopped at the point described there is enough moisture left so that, on stirring, the precipitate blends quickly with the acid and soon dissolves.

For the drying a large, rectangular, double-walled oven of the kind sold with oil or gas stoves is cheap and convenient.

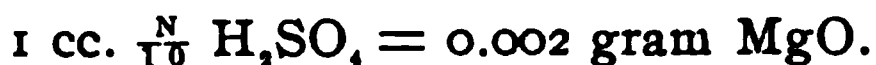
Unless magnesia determinations are constantly being made, it will often be more convenient to let the precipitates air-dry than to use an oven.

The tendency of magnesia to precipitate with iron and alumina and with calcium oxalate must be met by re-solution in hydrochloric acid and reprecipitation. When the amount of lime is considerable, it is best to burn off the first oxalate precipitate before dissolving in hydrochloric acid. By this means the oxalate is decomposed and the addition of ammonia alone does not cause its sudden reprecipitation. Even in the second precipitation, if the boiling is allowed to proceed longer than is necessary to make the finely crystalline calcium oxalate settle well, some magnesium oxalate is sure to precipitate, betraying its presence by its coarser texture. The solution for magnesia precipitation usually does and always should contain in the form of ammonium chloride the equivalent of 5 cc. of concentrated hydrochloric acid per 100 cc.

#### THE METHOD.

Add ammonia (sp. gr. 0.90), equivalent to one-tenth of the solution. Cool in water to 20° to 25° C. Precipitate by adding slowly with constant stirring a saturated solution of sodium ammonium phosphate, using 1 cc. for each 0.01 gram magnesium oxide. Stir vigorously for about five minutes or shake in a flask for an equal length of time. In the former case let the solution stand until the clarification of the upper liquid shows that the reaction is complete. In the case of flask precipitations,

if over 0.002 gram of magnesium oxide is present the solution may be filtered in fifteen minutes. Suction may be used if desired but if many solutions are to be filtered at once little is gained by its use. Use 10 per cent. ammonia wash (one part ammonia (sp. gr. 0.90) to nine of water). Deliver it preferably from an aspirator bottle placed about 4 feet above the bench. Wash by decantation as far as possible. Finally wash the precipitate which has gone on the filter, back into the beaker, stir it up with the ammonia wash and bring it again completely on the filter-paper. Wash once more, leaving the upper edge of the filter clear of precipitate so that it can be handled. Avoid assembling all of the precipitate in the apex but leave it fairly evenly distributed over the lower two-thirds of the paper. Allow the precipitates to drain and then transfer each in turn to a dry 5-inch filter-paper, allowing them to remain there open and face upward until the bulk of the moisture has been absorbed. After about three minutes transfer them to fresh dry filters, and in the case of heavy precipitates to a third set a few minutes later. Then place the filters on a shelf to dry at the temperature of the room or place filter-papers and backing on the grating of an air oven having a temperature of 50° to 60° C. After fifteen or twenty minutes in the oven or forty-five minutes in the air, watch for the time when the filters have dried inward half an inch from the margin. This appearance has been found to indicate that the evaporation has gone far enough to insure the expulsion of the free ammonia. The precipitates and filters may then be removed and placed in small dry beakers where they are treated each with a measured excess of decinormal sulphuric acid, and stirred until the papers are disintegrated and the precipitates dissolved. Two drops of a 0.1 per cent. alcoholic solution of methyl orange are then added. If this gives a clear decided pink, enough acid has been added. If it is only faintly pink the excess of acid is slight and some minute particles may have escaped solution. In such cases add five cc. more decinormal sulphuric acid and stir well. Finally dilute to about 100 cc. and titrate back with decinormal sodium hydroxide solution to the appearance of a clear yellow color, free from all suggestion of pink.





If filtrations have taken place during the latter part of the day the filters may be removed from the funnels and allowed to stand over night after which they are titrated as described.

The writer hopes that the simplicity and accuracy of the method may render it generally useful.

PITTSBURG, December 25, 1899.

## A PRELIMINARY COMMUNICATION UPON RICININE.

BY THOMAS EVANS.

Received January 2, 1900.

TUSON<sup>1</sup> obtained a substance crystallizing in plates which he called ricinine, by extracting castor beans, the seed of the *Ricinus communis*, with boiling water, filtering, evaporating to a thick sirup and again extracting with boiling alcohol.

Tuson states that ricinine is soluble in water and alcohol and very little soluble in ether and benzene, and that when heated with solid potassium hydroxide ricinine evolves ammonia.

He describes, but gives no analyses of crystalline compounds obtained by the action of nitric acid, mercuric chloride, and platinic chloride.

No salts with acids, with the possible exception of the nitric acid salt, were obtained by Tuson.

A few years later Werner<sup>2</sup> claimed that the ricinine of Tuson contained no nitrogen and was the magnesium salt of an acid with the formula  $C_{11}H_{10}O_{10}Mg \cdot 2H_2O$ . To this Tuson<sup>3</sup> replied that Werner had evidently investigated an entirely different substance, as his ricinine contained 20.79 per cent. of nitrogen.

Schulze<sup>4</sup> obtained a nitrogenous substance from the germinated seed of *Ricinus communis*, by extracting with alcohol, distilling this off, taking up the residue with water, treating with tannic acid and lead acetate, filtering, removing lead with hydrogen sulphide, and evaporating the filtrate to small bulk.

The impure product was purified by boiling the aqueous solution with animal charcoal and finally by crystallizing from absolute alcohol, from which it separated in small colorless prisms melting at 193° C.

<sup>1</sup> *J. Chem. Soc.*, 17, 195.

<sup>2</sup> *Jsb. d. Chem.*, 877 (1870).

<sup>3</sup> *Ibid.*, 877 (1870).

<sup>4</sup> *Ber. d. chem. Ges.*, 30, 2197.

Schulze says he is unable to identify this body with any known substance and calls it ricidine, assigning it the formula  $C_{11}H_{11}N_2O_2$ .

Pictet<sup>1</sup> gives ricinine the formula  $C_{17}H_{18}N_4O_4$ , but makes no reference to the original article from which this formula was obtained.

In the following investigation finely ground castor press cake, known as castor pomace, which was kindly furnished by The Brown Oil Co., of St. Louis, was used as a raw material. This was extracted by both Tuson's and Schulze's methods and in each case the same product was obtained, thus identifying the ricidine of Schulze with the ricinine of Tuson.

Tuson's method of extraction was found to be less satisfactory than that of Schulze, although the product so obtained was much lighter in color. It was found advantageous to modify Tuson's process, and use boiling toluene instead of alcohol to extract the residue from the evaporation of the aqueous extract. Upon sudden cooling of the toluene solution ricinine deposits on the sides and bottom of the containing vessel, in small, almost colorless prismatic crystals, which are frequently crossed and sometimes whetstone shaped, and which adhere tightly to the walls of the vessel.

The ricinine so obtained was purified by recrystallization from alcohol, from which it deposited in small plates frequently united to form rosettes. The melting-point was  $193^{\circ}C$ . and the analysis gave the following results, which agree very well with Schulze's figures :

	Calculated for $C_{12}H_{12}N_2O_2$ .	Calculated for $C_{16}H_{16}N_4O_4$ .	Calculated for $C_{16}H_{18}N_4O_4$ .	Schulze.		Evans.
Carbon	58.30	58.54	58.18	58.20	58.44	58.20
Hydrogen	5.26	4.88	5.45	5.15	5.31	5.06
Nitrogen	17.00	17.07	16.97	17.11	17.15	

In order to render the extraction by Schulze's method more complete a brass extractor of the Soxhlet type was constructed ; this held about 900 grams of pomace and was surrounded by a brass jacket, forming an air space between the two, through which the alcohol vapor could ascend to the return condenser, thus keeping the alcohol hot in the extractor. Later on it was found advantageous to place an additional jacket of asbestos around the brass one.

<sup>1</sup> Les Alcaloides vegetaux, 2nd. ed.

The dark brown alcoholic extract was treated according to Schulze's directions, giving a dark brown aqueous solution of ricinine from which yellowish brown crystals deposited on standing for twelve hours or longer.

Further evaporation of the mother-liquor gave a small amount of the substance; it was found impracticable to further concentrate the second mother-liquor, but upon diluting it with water, precipitating with subacetate of lead, filtering, precipitating out the excess of lead with hydrogen sulphide, filtering and evaporating to small bulk, more crystals of ricinine were obtained. An attempt to remove the brown color of the solution with animal charcoal, either before or after treatment with subacetate of lead, proved unsuccessful.

The impure product was purified by boiling its aqueous solution with animal charcoal. So prepared the substance showed a melting-point of  $193^{\circ}$  uncorr., and was evidently the same as the product obtained by the aqueous extraction of the pomace, as both gave the reddish purple color obtained by Schulze<sup>1</sup> by dissolving a few crystals in concentrated nitric acid, evaporating to dryness on the water-bath, taking up with water and again evaporating, and finally adding a drop of ammonia water.

To make sure that the product obtained by the extracting of the castor pomace was the same as Tuson obtained by the extraction of the beans, a quantity of these were extracted by his process and yielded a crystalline substance melting at  $193^{\circ}$  and was evidently the same as the products already described.

While it was found that neither sample of ricinine gave precipitates with silver nitrate, mercuric nitrate, or mercuric chloride, both gave a feathery crystalline product on long standing of a mixture of cold concentrated solutions of ricinine and mercuric chloride.

The chlorplatinate described by Tuson seems to be due to the presence of some more highly nitrogenous body; this seems the more probable when we compare Tuson's percentage of nitrogen (20.79 per cent.) with that found by Schulze (17.11 per cent.).

The writer has obtained the chlorplatinate referred to, but in each case it was with a ricinine which was manifestly impure as

<sup>1</sup> *Ber. d. chem. Ges.*, 30, 2198.

it melted partially at  $188^{\circ}$  and was completely melted at  $190^{\circ}$ – $191^{\circ}$ .

Further investigations of the double salt with mercuric chloride, the products obtained by the action of nitric acid and ammonia, are now in progress.

#### BROMINE DERIVATIVE.

When bromine or bromine water is added to a moderately concentrated solution of ricinine in water, the resultant red solution decolorizes very slowly, and upon heating on the water-bath to drive out the excess of bromine, long colorless radial needles separate, either immediately after the expulsion of the bromine or, if the solution be more dilute, upon evaporation.

The product was purified by repeated crystallization from alcohol, 95 per cent., and upon heating in a capillary tube darkened at  $220^{\circ}$ – $225^{\circ}$  C. shrinking at the same time and melted at  $229.5^{\circ}$ – $230^{\circ}$  under decomposition and evolution of gas. By moderately rapid heating the melting-point was found at  $232^{\circ}$ .

Qualitative tests showed the substance to contain both bromine and nitrogen. Upon boiling the aqueous solution with 10 per cent. silver nitrate there was a very slight darkening of the solution but no precipitation of silver bromide, thus showing the substance to be a bromide and not a salt of hydrobromic acid.

The same bromide was obtained upon treating a chloroform solution of ricinine with bromine in chloroform, as follows:

Two grams of ricinine were dissolved in about 200 cc. of chloroform by boiling in a flask connected with a return condenser; to this solution 12 cc. of a solution of 10 cc. of bromine in 50 cc. chloroform was added. After about a minute a considerable precipitate formed and settled to the bottom of the flask. (Ricinine floats on chloroform and it seems probable that the precipitate consists of the hydrobromic acid salt of ricinine, along with some dibromricinine.)

After boiling for ten minutes copious fumes of hydrobromic acid were evolved from the top of the condenser; boiling was continued for some time after these fumes ceased to come off, in all about an hour. The precipitate formed at first did not appreciably increase or diminish during the boiling.

The flask and contents were allowed to stand over night, the precipitate filtered off, washed with chloroform, and the filtrate

evaporated to dryness on the water-bath, the heating being continued until the residue had lost nearly all of its yellow color. The weight of the residue, impure dibromricinine, equaled 2.06 grams, and the dried precipitate weighed 1.82 grams.

When the precipitate was dissolved in boiling alcohol and the solution allowed to cool, prismatic crystals were obtained melting at  $192^{\circ}$  uncorr., which were evidently unchanged ricinine, as they gave the characteristic reaction with nitric acid and ammonia, while the bromide gave no such reaction.

The weight of ricinine recovered was about 1 gram.

The residue from the evaporation of the chloroform filtrate gave beautiful, long, brittle needles, generally radiating in clusters from several points, and whose length was largely dependent upon the diameter of the beaker and the depth of the solution. These crystals gave the same melting-point,  $230^{\circ}$  C., as those obtained by brominating in aqueous solution, which would seem to indicate that ricinine was an acid amide or perhaps a diureide. It was at first thought that it might be a substituted uric acid, but the fact that the murexide test fails to give the characteristic color, when performed with potassium chlorate and hydrochloric acid, or with dilute nitric acid, makes this seem doubtful.

The analysis of the recrystallized bromide gave the following results:

Water of crystallization, none.

I. 0.3525 gram substance, dried at  $120^{\circ}$ , gave 0.5173 gram carbon dioxide, and 0.1084 gram water.

II. The substance was recrystallized from absolute alcohol and 0.2055 gram substance, dried at  $120^{\circ}$ , gave 0.3000 gram carbon dioxide, and 0.0561 gram water.

	Calculated for $C_{16}H_{14}Br_2N_4O_4$ .	Calculated for $C_{16}H_{16}Br_2N_4O_4$ .	I.	II.
Carbon	39.53	39.99	40.02	39.81
Hydrogen	2.88	3.27	3.41	3.03
Bromine	32.92	32.79	32.343	....
Nitrogen	11.52	11.42	12.28	11.97

The discrepancy between the results obtained and the theory is probably due to impurity in the form of ricinine. Lack of substance has prevented a more careful separation of the dibromide

from possible impurity; but with more substance more satisfactory results are expected.

The formula  $C_{11}H_{11}N_2O$ , proposed by Schulze does not suit the bromine derivative as well as the ones suggested above, as  $C_{11}H_{11}BrN_2O$  calls for 24.54 per cent. of bromine and  $C_{11}H_{11}Br_2N_2O$  for 39.50 per cent.

Ricinine dibromide is soluble in about 200 parts of 93 per cent. alcohol and in practically the same amount of water; it is rather less soluble in chloroform. From dilute solutions in alcohol or water it crystallizes in long needles, while from more concentrated solutions it is obtained as a mass of short, silky, white needles.

So far all attempts to make a bromide containing less bromine have proved unsuccessful, the same product being obtained with varying amounts of bromine.

Ricinine dibromide is soluble in hot, dilute, or concentrated hydrochloric acid and separates out unchanged on cooling. When treated with concentrated nitric acid and ammonia as described under ricinine, it gives no characteristic color.

Its aqueous solution appears to be neutral, and it was found impossible to prepare double salts with platinic or auric chloride.

#### OXIDATION OF RICININE.

Schulze states that upon oxidizing ricidine with potassium bichromate and sulphuric acid an odor of hydrocyanic acid was obtained, but does not mention other oxidation products.

Upon treatment of an alkaline solution of ricinine with potassium permanganate, the latter was almost immediately reduced, the reduction being accompanied with a faint odor of hydrocyanic acid. Upon filtering off the oxide of manganese a colorless solution was obtained, which became red with a yellow fluorescence upon acidifying with hydrochloric acid; when heated on the water-bath the solution became more intensely colored, and upon evaporation and subsequent cooling, beautiful, long, wavy, salmon-pink needles separated. These proved to be free from inorganic matter and were completely decolorized when their aqueous solution was boiled with animal charcoal.

The oxidation was carried out as follows:

One-half gram ricinine was dissolved in 20 cc. of boiling water

to which 5.5 cc. of approximately normal potassium hydroxide were added. After cooling to 17° C. a solution of potassium permanganate, containing 5.8 grams of the solid in 320 cc. of water, was slowly added until a further addition produced an evolution of a few bubbles of gas; in all 16 cc. of the permanganate were added.

The flask and contents were then allowed to stand for five hours; the oxide of manganese, which had settled, was filtered off after being washed by decantation. The filtrate and washings equaled 100 cc.

The colorless alkaline solution was heated on the water-bath, and made faintly acid with hydrochloric acid, when a few bubbles of carbon dioxide were evolved and the solution became red. Upon evaporation until crystals were deposited on the sides of the dish at the level of the liquid, and then allowing to stand, 0.27 gram of pink silky needles were obtained, melting, after previous blackening, at 269.5°. After repeated boiling of the aqueous solution with animal charcoal, the crystals were obtained snowy white; it was impossible to remove all of the color from the mother-liquor.

The purified substance melted at 279°—280°, becoming black several degrees below the melting-point.

The aqueous solution of the oxidation product is acid to litmus paper, and forms crystalline salts with alkalies as well as with silver nitrate. A test for the degree of acidity, using phenolphthalein as an indicator, gave the following results:

0.1079 gram acid dissolved in 50 cc. of water required 7.1 cc. standard alkali containing 0.001971 gram NaOH per cc., for neutralization; or 0.00805 gram Na, which equals 7.46 percent. Na.

The acid contains nitrogen, and on evaporation with nitric acid and moistening with ammonia, gave the reddish purple color characteristic of ricinine, but to a lesser degree,—hence the thought that this may be due to impurity in the form of unoxidized ricinine.

A second portion of 1 gram of ricinine was oxidized in the manner already described, made acid with hydrochloric acid, and concentrated until 6 grams of reddish needles, mixed with dark red prisms, were obtained; these were filtered off and boiled with benzene for several hours, when a reddish yellow solution

with a green fluorescence was obtained, the prismatic crystals being dissolved while the needle-like crystals appear to be quite insoluble. Upon evaporation of the benzene solutions red prismatic crystals were obtained which became colorless with ammonia, and on evaporation of the solution so obtained gave a colorless crystalline mass.

The difficulty in preparing even small amounts of ricinine has materially interfered with the process of the investigation. The writer is now germinating seed in the dark, and hopes to be able to contribute further in the near future.

UNIVERSITY OF CINCINNATI,  
December 29, 1899.

### NOTES.

*Retention of Moisture by Asbestos.*—In the use of the Gooch crucible error may result from ignoring the fact that asbestos (some asbestos at any rate) retains moisture with great tenacity, so that after being dried at 100° C. to constant weight, the Gooch apparatus will suffer a further and notable loss of weight upon ignition over a Bunsen burner.

	Grams.
1. Dried one hour at 100° C., weighed.....	21.0452
Again dried one hour at 100° C., weighed.....	21.0450
Then ignited ten minutes, weighed.....	21.0441
2. Dried one hour at 100° C., weighed.....	21.0436
Then ignited five minutes, " .....	21.0429
3. Dried one hour at 100° C., " .....	21.0418
Again dried one hour at 100° C., weighed .....	21.0418
Then ignited five minutes, weighed .....	21.0409
4. Dried two hours at 100° C., " .....	20.7304
Then ignited one-fourth, weighed.....	20.7293
5. Dried three hours at 103° C., weighed. ....	20.8250
Then ignited one-fourth hour, weighed .....	20.8246
6. Not dried in air-bath.....	.....
Ignited five minutes.....	21.0950
Then ignited again one hour .....	21.0944
7. Asbestos in larger quantity from a Hirsch funnel dried in a platinum crucible six hours at 90°–100° C.	20.2828
Then ignited one hour .....	20.2811
8. Ignited in a platinum boat in porcelain combustion tube in current of oxygen, then dried three hours at 100° C .....	21.1742
Then ignited one hour.....	21.1726



The asbestos used in these experiments was, of course, previously ignited and purified.

It is therefore necessary, when the weight of a dried precipitate is to be found, either to get the preliminary weight of the Gooch crucible by drying the same length of time, and at the same temperature as is intended with the precipitate; or much more conveniently, to find, once for all, the weight of the moisture retained by the dried Gooch crucible, and make the necessary correction when getting weights of precipitates.

GEORGE AUCHY.

*The Determination of Graphite by Loss.*—The figures given in the above note show that it is necessary to observe precaution in determining graphite in pig iron by the method of loss upon ignition, if the operator prefers the use of asbestos to that of a weighed paper disk or to counterpoised filters. Although the proposers of this method of determining graphite (Eggertz, Tamm, Crobaugh, Dougherty, Rodgars) are unanimous in directing the use of weighed paper for filtering, asbestos seems preferable for the reason that by its use the time and labor of drying and weighing the paper disk, or of drying and counterpoising the filters, is saved. With asbestos no weight is taken except that of the Gooch crucible plus graphite, etc., after drying, and again after ignition, the loss representing graphite. In the absence of a Gooch crucible the filtration may be made in a Hirsch funnel, or a Shimer funnel, and the asbestos and graphite then transferred to an ordinary crucible with the graphite part of the asbestos pressed against the wall of the crucible, as is also done when a Gooch crucible is used.

In using this method of loss upon ignition (filtering through counterpoised filters) Crobaugh obtained somewhat variable results (3.53 per cent. to 3.75 per cent.) which he attributed chiefly to non-homogeneity of the drillings. The presence of hydrated silica could not serve as an explanation, because the elimination of the silica by the addition of hydrofluoric acid during solution of the drillings, is a distinguishing feature of his method. The writer of this note also obtained varying results by the method, which, in his opinion were due, not to any lack of homogeneity in the drillings (mixed as they were by the aid of alcohol as recommended and found necessary by Shimer), nor

to the presence of gelatinous silica not completely dehydrated by the heat used in drying the graphite (Drown being strictly followed in dissolving the drillings as in phosphorus determinations), but probably to the fact that graphite thus obtained is not always pure carbon, but contains sometimes other combustible matter—combinations of hydrogen, oxygen, nitrogen, and sulphur in some form. For smaller percentages the method may serve. By combustion as usual, we obtain 3.21 per cent., 3.24 per cent.; by loss upon ignition, 3.35 per cent., 3.36 per cent., 3.38 per cent., 3.20 per cent.

That gelatinous silica, if present, is not dehydrated by the drying of the graphite, was found by Tamm. An experiment by the writer showed 0.0094 gram water retained by about 0.13 gram gelatinous silica after being dried as graphite is dried.

GEORGE AUCHY.

*The Persulphates of Rubidium, Cesium, and Thallium.*—In the October part of this Journal,<sup>1</sup> there is a short paper by Foster and Smith on the above subject. As I have recently prepared and partially investigated these salts, I consider it advisable to publish the present note, retaining details for a paper to be published later.

The rubidium and cesium salts were prepared from ammonium persulphate by double decomposition, purified, and recrystallized. The crystals are not isomorphous with those of the potassium salt (triclinic), but with those of the ammonium salt (monoclinic). As mixtures of the potassium salt with the others have been obtained in well-formed monoclinic crystals, notwithstanding a great preponderance of potassium salt, it is evident that we have here to deal with an isodimorphous group.

The thallos salt has not yet been obtained pure, but mixtures of it with ammonium persulphate have been obtained in crystals isomorphous with the above monoclinic group. As the electrolysis of thallos sulphate solution would present interesting peculiarities, owing to the existence of thallic compounds, it was decided to investigate that subject also. It was found necessary to delay this, however, to permit of a preliminary investigation of thallic sulphate and its double salts, which is at present being carried out. Thallos persulphate,  $\text{Tl}'_2\text{S}_2\text{O}_8$ , is isomeric with thallos thallic sulphate,  $\text{Tl}'\text{Tl}'''(\text{SO}_4)_2$ , or  $\text{Tl}_2\text{SO}_4\text{Tl}_2(\text{SO}_4)_2$ .

UNIVERSITY OF EDINBURGH,  
October, 1899.

HUGH MARSHALL.

<sup>1</sup> This Journal, 21, 934 (1899).

## OBITUARY.

SIR EDWARD FRANKLAND.

WE are again called upon to note the departure of a co-worker and master in our chosen field of science. Eulogy is not necessary. The good he has achieved lives after him, and we would merely note that the researches of Sir Edward Frankland, extending over a period of thirty years, relate to work in pure, applied, and physical chemistry. Those in pure chemistry were conducted at first in the laboratories of Playfair, Bunsen, and Liebig. They include subjects related to each other as follows: the conversion of the cyanogen group into the carboxyl group; the change of the alkyl cyanides to the corresponding organic acids, the saponification of ethyl cyanide was announced by Edward Frankland and Hermann Kolbe when they were fellow assistants in Playfair's laboratory in 1845. Although this reaction was not then pursued beyond the monobasic acids, others applied it successfully in other directions. Then followed the action of metallic potassium upon ethyl cyanide and the polymerization of the latter, the isolation of the organic radicals, and the discovery of the organo-metallic compounds. Of these, which were investigated by Frankland throughout his scientific career, were zinc methyl and zinc ethyl, in the study of which the author remarks: "I had not proceeded far in the investigation of these compounds before the facts brought to light began to impress upon me the existence of a fixity in the maximum combining value or capacity of saturation in the metallic elements which had never before been suspected." The ready introduction of negative chlorine into bodies for a more electropositive constituent is a fact to which we give little thought. "The inverse process" in the day of Frankland "had been successfully accomplished in comparatively few cases." Through zinc methyl he succeeded in substituting methyl, ethyl, etc., for electronegative constituents, thus "opening up a most extensive and absolutely new field of research."

Next came the syntheses of acids of the lactic series, of the acrylic series (aiming here to produce the higher fat acids by direct synthesis from acetic acid), with the formation of ethers and ketones.

In applied chemistry Frankland studied the "hydrocarbon" process of gas-making and contributed much to the knowledge of gas manufacture. He also studied magnesium as a source of light.

In connection with his studies of the water supply of London he developed new and accurate methods for the determination of the amount of organic carbon and nitrogen in potable waters. As a member of the Royal Commission on the Pollution of Rivers he conducted, during a series of years, most exhaustive researches upon the question of water supply. Frankland also gave attention to the spectra of gases and inquired into the source of muscular power. He presented four or five papers relating to "climate," discussing the physical cause of the glacial epoch. Crooke's radiometer and colored solar halos also engaged his earnest thought.

The preceding lines indicate in a measure the scientific activity of the great investigator whose earthly career ceased on August 9, 1899, at the age of seventy-four years.

BOSTON MEDICAL

DEC 4 1917

WM. A. NOYES,  
A. B. PRESCOTT,  
EDGAR F. SMITH,  
*Committee.*

LIBRARY NEW BOOKS.

**DETERMINATION OF RADICALS IN CARBON COMPOUNDS.** BY H. MEYER. Authorized translation by J. BISHOP TINGLE. New York: John Wiley and Sons. London: Chapman and Hall. ix + 133 pp. 12mo. Cloth. Price, \$1.00.

This book is a translation of the original German edition with various corrections, additions, and changes in arrangement made partly by the author and partly by the translator. The successful methods known at present for the determination of organic radicals have been collected in the five chapters of this little volume, which deal with the following topics: Chapter I.—Determination of hydroxyl; Chapter II.—Determination of methoxyl, ethoxyl, and carboxyl; Chapter III.—Determination of carbonyl; Chapter IV.—Determination of the amino, nitrile, amide, imide, methyl imide, and ethyl imide groups; Chapter V.—Determination of the diazo group, the hydrazo radical, the nitro group, the iodoso group, the iodoxy group, the peroxide group, the iodine number.

The book contains then in compact form much valuable material that the student must ordinarily gather from various texts and periodicals. References to original articles are given. The improvements and additions have brought the book up to date. The translator has done his work in a commendable way. The excellent work of the publishers is too well-known to require further comment.

LOUIS KAHLENBERG.

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### ARE FURTHER EXPERIMENTS NEEDED FOR DETERMINING THE ATOMIC WEIGHT OF OXYGEN?

BY EDWARD W. MORLEY.

THE precision of experiments on the atomic weight of oxygen has been gradually so much increased that, in some cases, the mean error of a single determination is less than 1 part in 10,000. The agreement of different series of experiments is not so good, but if the work of different experimenters agreed well, the question, how accurately do we really know the atomic weight of oxygen, is not one which we can readily answer. Neither the concordance of the experiments of a given series, nor the agreement of the results of series of experiments by different observers, can excuse us from search for sources of error. All sciences which have to do with measurement afford sufficient instances of the fact that our conclusions are to be received with a certain suspense of judgment. And chemistry well illustrates that he is wise whose assertions regard the possibility of finding at some time evidence to the contrary.

The history of experiment on the atomic weight of oxygen affords an interesting example of the fact that neither the con-

<sup>1</sup> President's address, delivered before the New Haven Meeting of the American Chemical Society.

cordance of individual observations nor the agreement of different experimenters proves that a measurement is right. Toward the middle of the century, Dumas made his classic experiments on the composition of water. The probable error of a single experiment was, in round numbers, 1 part in 400, so that the probable error of the average of the 19 famous experiments was 1 part in 2250. Now, this means that his final value was not likely to differ more than a certain small quantity from the result of the repetition of even a very large number of experiments made in the same way, with the same skill and care. But as to the difference between this result of the 19 experiments and the unknown true value, we are told absolutely nothing by the proposition that the probable error of Dumas' result was 1 part in 2250. It is a commonplace to say, that the calculation of the probable error of a series of experiments does not show how nearly the result approaches the truth, but how near it is to the result of a greater number of similar experiments. It decides, not how nearly we approach the desired goal, but whether it is useful to persevere by the present method of approach. Dumas made 19 observations, and got the value, 15.96, with a probable error of 0.007 ; that is, if he had made 100 or 1000 experiments, it is unlikely that the final result would not have been between 15.95 and 15.97, and very unlikely indeed that it would not have been between 15.94 and 15.98. But he would never have obtained a value near that which now commands confidence.

It is interesting to recall that there is hardly any instance on record where the judgment of an experimenter as to the degree of approximation to the truth attained in his work has been better justified than in the case of Dumas' classic experiments. As we all remember, towards the end of his work, there was discovered in his own laboratory a source of error, not easy to eliminate, which had affected all his determinations. The amount of the error was not a fixed quantity, and no numerical correction could be applied to the results of observation. Dumas accordingly gave to the public the uncorrected and unmodified results of experiment. But he also stated his opinion as to the degree in which his results approximated, not to the mean of a larger number of experiments of the same kind, but to the unknown and unattainable true value. He expressed the hope that his

value would be found not more than one part in 200 from the result of those subsequent experiments which should be thought satisfactory ; and it is by just 1 part in 200 that his value differs from that which is now accepted.

So the concordance of Dumas' experiments did not prove that his result was right ; neither did the agreement of experiments by different observers. Erdmann and Marchand made eight experiments by a method like that of Dumas, with some modifications. Their result was 15.973, with a probable error of 0.011. This value differs from that of Dumas by less than the sum of the probable errors, so that that agreement is perfectly satisfactory. So, also, Regnault determined the ratio of the densities of oxygen and hydrogen, from which was computed the atomic weight of oxygen as 15.963, with a probable error of 0.004. The results of Dumas, of Erdmann and Marchand, and of Regnault, show a very good agreement. But all of them, and the mean of all of them, we now know to be in error by 1 part in 200.

I adduce this example, somewhat in detail, to enforce the proposition that we must not excuse ourselves from looking for error because observations agree. We have experiments which give the atomic weight of oxygen with a probable error of 1 part in 50,000, but do we know it within 1 part in 1,000? Each individual experimenter whose work would now be regarded as free from known and tangible error, agrees fairly well with the mean of all. For instance, Noyes' results show that degree of concordance which would justify us in expecting that, if he were to make 100 or 1,000 experiments, his final mean would be as likely as not to be larger or smaller by 1 part in 9,500, and his result differs from that which we accept by 1 part in 900. So Cooke and Richards assign a value which is just as likely as not to be within 1 part in 8,000 of the result which they would have obtained by multiplying observations ; and it differs from that which we accept by 1 part in 1,500. But do we know that their means, and the means of all published results taken together, are not in error by 1 part in 900? The concordance of the results of a single experimenter, and the agreement of different experimenters, does not justify us in asserting that we do.

In determining the atomic weight of oxygen, it has been somewhat difficult to determine directly all three of the quanti-



ties involved, and so to make what Stas called a *complete* synthesis. Berzelius, Dumas, and Erdmann and Marchand, weighed oxygen and weighed water, thus determining hydrogen by difference. More recently, Dittmar and Henderson, and Leduc used the same method. Cooke and Richards, and Keiser, weighed hydrogen and weighed water, while Rayleigh and Noyes weighed hydrogen and weighed oxygen. Any proceeding which weighs hydrogen directly has a great advantage in precision; different determinations in a given series agree better among themselves, and the series of different experimenters also agree better. But there is also a second, more important advantage. We have reason to believe that the constant errors involved in weighing hydrogen are small, for it is possible to obtain hydrogen with less than  $\frac{1}{10,000}$  or even  $\frac{1}{20,000}$  of its weight of impurity. There is no difficulty in weighing oxygen or water with accuracy, so if we weigh hydrogen and also weigh either oxygen or water, we may hope for a near approximation to the true value of the ratio sought.

We may hope, but we cannot *know*. We may believe that our hydrogen is pure, and that there was no error through leakage. But an unsafe stop-cock might make the apparent weight of the hydrogen in a series of experiments seem always smaller than the fact, and might yet leave the individual experiments so concordant with each other as to seem trustworthy.

If, however, we can weigh hydrogen and can weigh oxygen, and then combine them and weigh the water produced, we can at least give a better reason for our hope, if we find that the product is nearly equal to the sum of the components. The manipulation in this case is costly, and is so difficult, and involves so many minute details, that not many have patience and time sufficient for it, so that no great number of such complete syntheses has been made, and these few were made in conditions but little varied. When such complete syntheses shall have been made by different observers, with those variations of apparatus and method which may seem wise to them, we shall be able to judge of the magnitude of the errors to be feared. If such results are not concordant, we shall have much to learn as to sources of error; but we now see some reason to expect that they will not be discordant. However, even if they are not dis-



cordant, we are not to excuse ourselves from further study of sources of error.

Before repeating determinations so troublesome, and before studying unknown sources of errors not yet detected, the experimenter should receive all possible assistance from chemical theory and from criticism. For some that criticism may be most profitable which is friendly and sympathetic; but, for the experimenter, the value of the criticism depends on the knowledge and the acuteness of the critic. Dr. Hinrichs published, some five years ago, a criticism of all determinations and computations of atomic weights since Dumas. As is well known, he is a most strenuous and insistent supporter of Prout's hypothesis. Looking hastily through the volume, there was found, towards the end, evidence that its author was one of those who, some thirty years ago, discerned that which, in the hands of Mendeléeff, became the periodic law. It seemed possible that one who had early seen some indications of this law might, perhaps, also have discerned, even if obscurely, some principle relating to atomic weights. I therefore once spent some time and pains in carefully reading the book, and considered at length those passages, which, if any, contained valid criticism of the views which are generally accepted.

Hinrichs believes that the mean of a series of determinations of an atomic weight cannot give the true value sought. This proposition he deduces from a mathematical discussion. He believes that as larger and larger quantities are taken in our analytical operations, the results differ regularly from ideal accuracy; sometimes the difference continually increases as the quantity taken increases; sometimes the difference increases to a maximum and then decreases again. The proper computation of an atomic weight then, according to Hinrichs, consists not in taking the mean of different observations, made with different weight of materials, but in determining the limit towards which the series converges as the weight taken decreases. A good illustration is given: we cannot determine the weight of a new coin by weighing any number of old coins; every coin is worn and therefore light, and the mean weight of any number whatever is therefore necessarily below the mean weight of new coins. But if we weigh old coins and note the date of each, we may

take the mean weights for each year separately. If we examine coins enough, these means when plotted as the ordinates with the years as the abscissas, will give us a "fairly regular curve, lowest for the oldest coins, gradually rising towards a *limit* which they would not quite reach. This higher limit would evidently be the mean weight of the new coin."

This is an intelligible proposition. It seemed to me worth while to examine it, for to this proposition one of the most enthusiastic and most active supporters of Prout's hypothesis, a man not lacking in shrewdness or ability or learning, has entrusted the defense of his favorite belief.

He asserts that an atomic weight as determined by experiment is variable, that it depends on the amount of substance taken for the analysis or other operation, and that it varies in a continuous and regular manner. His proposition is, that an atomic weight as determined by experiment is a function of the weight of substance taken. Is there any evidence in favor of it?

I answer, first: Theory does not afford any evidence for it. Hinrichs deduces this proposition from theory by a discussion which is mathematical in form. Whether the proof is sound need not be considered, for his theory does not attempt to show the order of magnitude of the regular and continuous variations which are affirmed to depend on the weight of substance taken, and to show whether they can be separated from the irregular and discontinuous errors due to accident. We are sure that accidental errors exist; we may concede, for argument, that regular and continuous variations also exist; but this is far from implying that the actual errors in a given set of experiments will be largely or even perceptibly of the latter kind. Theory shows that there is a diurnal tide in the atmosphere; but theory does not show that the differences noted in a series of ten observations of the barometer at different hours of the day will follow the law of the diurnal tide.

But, secondly: Facts do not agree with the proposition. The accidental errors of the most precise experiments yet made are so much greater than any *systematic* variations, that nothing but accidental variations can be detected. To prove this, let us consider Stas' synthesis of silver nitrate from pure silver. This is one of the most important determinations ever made; Hin-

richs has discussed it twice in his volume ; he asserts that the ratio of silver nitrate to silver found in each analysis depends on the weight of silver taken, and twice draws curves to show this. I assert, on the contrary, that the errors, which average only 1 part in 40,000, are purely accidental, and that they follow no law. This can be proved by proving that the ratios obtained depend on any other quantities selected by accident just as much as they depend on the weights of silver taken. Hinrichs plots the results of the ten determinations, using for abscissas the weights of silver taken, and so obtains tolerable curves. I plotted the same ten observations, using for abscissas not the weights of silver taken but ten numbers selected by *sortes Virgilianae*, and get curves quite as tolerable as before ; and this I did with ten different sets of abscissas, all selected by pure accident. Now, quantities which depend on any one of eleven sets of abscissas, ten of which are selected by accident, are themselves accidental in their variations, and the variations follow no law. So far as the facts are examined, they give no evidence in favor of Hinrichs' proposition ; we have seen that theory is equally chary of her support, and we may safely dismiss the suspicion that any source of systematic error can be detected in deducing atomic weights from the means of good experiments.

Within the limits of convenience, it is well to vary the amount of substance taken in analytical determinations. This has been a frequent practice in the finest investigations. But that this practice derives any support from the so-called "limit method" cannot be conceded.

This criticism, this attempt at a theory, then, removes no obstacles and reveals no threatening pitfalls. If we desire a firmer foundation for our system of atomic weights, we must simply enlarge the experimental basis of our knowledge.

If it is only by further experiment that we can make surer of the atomic weight of oxygen, we are to consider what kind of experiments is most desirable. It is chiefly for the sake of eliciting discussion on this point that the subject of this address has been chosen.

Our present value for the ratio between oxygen and hydrogen rests on one single chemical combination, and upon two processes for determination. The first is, the synthesis of water from its

components. The second is, the determination of the densities of the gases and of their volumetric ratio. Let us consider these in order.

What synthetic experiments should be repeated? We are met by the fact that a complete synthesis, in which hydrogen and oxygen and water are all three weighed, can be made with errors only about one-fourth as large as the errors in any of the syntheses where only two substances are weighed out of the three concerned. Other things being equal, then, this process is by far the most promising. But, so far it has been carried out adequately by only one experimenter. Conditions were varied somewhat, it is true, but by no means so much as they would be varied if the same person repeated the experiments after an interval of years; by no means so much as if others were to undertake such complete syntheses. Lately, Keiser has devised a process which varies in many particulars from that already executed; it is very desirable that he should make a series of experiments, after adequate study of sources of error and of means of avoiding them. It is also desirable that, if possible, the original process of complete synthesis should be repeated with the little modifications which time is sure to introduce. These two would be enough, as far as synthesis is concerned; unless, indeed, through the invention of another process by a third experimenter, we could have still more. Other syntheses of water than by a *complete* synthesis seem less likely to be of much service, except as a school of experimentation.

What further work is desirable on the ratio of densities and of combining volumes of hydrogen and oxygen? Three constants are involved: the density of oxygen, the density of hydrogen, and the volumetric ratio.

The density of oxygen is known with a probable error of about 1 part in 50,000. It is very probable that no number whatever of further determinations would change this value by 1 part in 10,000. No further work upon this density seems at present desirable, except that whoever determines the density of hydrogen cannot well fail to determine that of oxygen also.

The density of hydrogen demands further experiment. It is possible to make, by some one of three or four slightly different processes, a series of experiments whose average variation shall

be less than 1 part in 3,000, or 5,000, or even 10,000; but different series do not agree sufficiently with each other. We are far from knowing the density of hydrogen so well that more observations might not change our value by 1 part in 2,000 or 3,000. It is very desirable that further observations should be undertaken by at least two different methods. In one method, hydrogen should be weighed while absorbed in palladium, should be then transferred to a measuring apparatus without the use of stop-cocks, and should be there measured. This process should be repeated with measuring apparatus of varied volumes. In another method, hydrogen should be weighed after Regnault's method, in a counterpoised globe, but with such precautions that leakage through a stop-cock, and contamination with vapor of mercury, should be excluded. The globe should be exhausted till the remaining air is a small fraction of a millionth, should be sealed off from the pump, and should be connected with a condenser at the temperature of liquid air, so as to remove mercurial vapor. After this hydrogen is to be admitted without the use of stop-cocks. The manipulation is not difficult, and the method would confirm the results of the previous method.

The ratio of the combining volumes of hydrogen and oxygen is not known with the degree of confidence which is desirable. The history of the matter is not an interesting one. Further continuance of the two series of experiments on which the present value depends would be most unlikely to change it by 1 part in 10,000, for its probable error is 1 part in 40,000. But one of the experimenters has obtained results differing from that finally adopted by as much as 1 part in 220. The other experimenter has entirely discarded the result of one series and replaced it, not by a better series of the same kind but by one of a quite different nature, not carried to its proper completion, and accordingly reduced by the use of the constants of van der Waals' equation. It is desirable that experiments be made to furnish means for a new reduction by measuring the change of volume when 2 volumes of hydrogen and 1 volume of oxygen are mixed, being at the same pressure before and after mixing. This experiment has lately been made by Berthelot, whether with sufficient precision for the purpose is not known at this moment. It is also desirable that the ratio of the combining volumes of

oxygen and hydrogen should be measured with the gases contained in vessels of the dimensions of those used for obtaining their densities.

If these syntheses and these studies of ratios of densities and combining volumes should agree as well as it is safe to expect, we should know the atomic weight of oxygen as confidently as we can know it while the value rests on a single chemical process, the combination of the two gases to form water.

But this is not so much as is desirable. We know the atomic ratio between silver and oxygen with considerable confidence, because this rests not on a single chemical process but on eight different chemical processes, which give eight independent results, and because these eight results agree. Is there, then, any chemical process by which the atomic ratio of oxygen and hydrogen can be determined, other than the analysis or synthesis of water? Is there any element whose atomic ratio to oxygen is well known, whose ratio to hydrogen is capable of accurate direct determination?

It is probable that, given an adequate equipment, the direct ratio of hydrogen to chlorine, of hydrogen to sodium, of hydrogen to magnesium, or of hydrogen to aluminum, could be determined with sufficient precision for the purpose, provided that the ratio of chlorine to oxygen, of sodium to oxygen, of magnesium to oxygen, and of aluminum to oxygen are well enough known. This may not now be the case with aluminum or magnesium, but is the case with chlorine and with sodium, whose atomic ratios to oxygen may be fairly assumed to be known within 1 part in 2,500. If, now, we can determine the ratio of chlorine to hydrogen, or of sodium to hydrogen, to 1 part in 5,000, we could compute, by a new method, the ratio between hydrogen and oxygen. If this should agree with the present value, within some such quantity as 1 part in 2,000, we should be as confident of the truth of our value of the atomic weight of oxygen as we can well hope to be.

The difficulties in making a complete synthesis of hydrochloric acid are not small, nor are they all well understood. Some unexpected circumstance may be prohibitive. But there is good reason to hope that 3 or 4 or 5 grams of hydrogen could be

weighed, that a nearly equivalent quantity of chlorine could also be weighed, that the two could be combined, and that the product could be weighed. One serious difficulty would be found in attempting to prepare pure chlorine, but the difficulty does not seem insuperable. The manipulation of the corrosive element requires invention, but seems not difficult. For the collection of the hydrochloric acid in a weighable form, there seem to be alternative methods, not very troublesome of execution, unless unforeseen difficulties are encountered. If the ratio between hydrogen and chlorine could be determined to 1 part in 5,000 or to 1 part in 10,000, it would be a very interesting addition to our list of known constants, most helpful in establishing confidence in the ratio between oxygen and hydrogen.

So, also, if sodium can be prepared of sufficient purity, or of sufficiently constant impurity, it seems possible to weigh 100 or 200 grams, to act on it with water in such a way as to produce a slow evolution of hydrogen, and to determine the weight of this hydrogen by loss. Whether sodium can be obtained sufficiently free from absorbed hydrogen and whether it can be prepared for weighing without attacking the vessels which contain it, are questions which need further experiment. It is probable that a vessel of platinum-iridium alloy could be made which would make success almost certain, but at considerable cost. In this case also, if the ratio between sodium and hydrogen can be determined to 1 part in 5,000, or 1 part in 10,000, the result would inspire confidence, or, if it must be, distrust, in our present value for the ratio between oxygen and hydrogen.

These suggestions, necessarily tentative in their nature, are submitted to the American Chemical Society, in the hope of obtaining from those who do me the honor to listen to them or to read them, expressions as to the desirability of making experiment in the lines described, and discussions of the new methods indicated as possible.



## A PRELIMINARY STUDY OF THE COBALTICYANIDES.

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SEVERAL years ago during the course of an investigation of the ferrocyanides of zinc and manganese,<sup>1</sup> it was suggested that a study of the reactions between potassium cobalticyanide and solutions of metallic salts might be of interest and that, possibly, this compound might be found useful as a reagent in either qualitative or quantitative analysis. A careful search through the literature showed that the subject had not been thoroughly investigated; that the cobalticyanides of many metals were unknown and that the properties, especially the solubilities, of the known cobalticyanides were but incompletely recorded. Apparently no work has been done on these compounds for many years, while most of the investigations bear dates prior to 1857.

The general procedure adopted in this work was:

*First.*—To try the action of a half-normal solution of potassium cobalticyanide<sup>2</sup> on half-normal solutions of all the common metals. They were first added to each other in equal quantities and the filtrate tested to see which reagent was in excess; and, having found the amount of potassium cobalticyanide needed to precipitate a given metal, to work in subsequent experiments with quantities which gave a slight excess of the precipitant. Although these solutions were only approximately half-normal, they were made with sufficient care to distinguish in the resulting precipitates between a normal cobalticyanide and a double potassium-metallic cobalticyanide. The indications show that in nearly every case a normal salt is produced by a reaction of simple double decomposition.

*Second.*—The solubility of the precipitates so obtained was tested in every instance in nitric, hydrochloric, sulphuric, acetic, and oxalic acids, in ammonium hydroxide and caustic potash; in all cases both cold and hot.

<sup>1</sup> This Journal, 19 547 (1897).

<sup>2</sup> Based on the hydrogen equivalent in grams per liter.



These tests were made by adding the acid or alkali to the original liquid containing the precipitate, and, in each instance, an amount of solvent equal in volume to the original liquid was employed. A few precipitates were filtered and their solubilities tested in concentrated acids.

The special solutions used were of the following strengths:

$K_3Co(CN)_6(N/2)$ 55.52 grams per liter.				
$HNO_3$	(1 : 3)	sp. gr.	1.135	= 22 per cent.
$HCl$	(1 : 1)	" "	1.10	= 20 " "
$H_2SO_4$	(1 : 4)	" "	1.20	= 28 " "
$HC_2H_3O_2$		" "	1.03	= 22 " "
$H_2C_2O_4$	saturated solution			= 10± " "
$NH_4OH$	(1 : 2)	sp. gr.	0.96	= 10 " " $NH_3$ .
$KOH$		" "	1.11	= 10 " " $K_2O$ .

No highly colored or characteristic precipitates have as yet been found which can be employed as indicators to show an excess of potassium cobalticyanide, nor do the precipitates settle readily enough to allow this point to be determined by cautious additions of cobalticyanide to the clear supernatant liquid or by spot tests. In every precipitation the potassium cobalticyanide was added to the metallic salt solution and the presence of either substance in excess had usually to be determined in a few drops of the filtrate from the resulting precipitate. The experimental part of our work will show that, in general, the cobalticyanides insoluble in water, are also insoluble in and unaffected by acids, but are soluble in or decomposed by alkalies. None of them are decomposed by boiling as is the case with several ferricyanides. There is little similarity in either solubility or appearance between the corresponding ferri- and cobalticyanides. The metals except those of the alkalies and alkaline earths were taken up in their qualitative sequence, beginning with the silver-lead-mercury group.

*Silver Cobalticyanide.*—When equal volumes of half-normal silver nitrate and potassium cobalticyanide solutions are mixed, the silver is completely precipitated as silver cobalticyanide, a white curdy precipitate, which settles and filters well; is insoluble in all the acids used, being transposed by hydrochloric acid; is soluble in ammonia and decomposed by potassium hydroxide giving a precipitate consisting mostly of silver oxide.

*Lead Cobalticyanide*.—Neither lead acetate nor nitrate are precipitated by potassium cobalticyanide, either in neutral or acid solutions. Zwenger<sup>1</sup> made it from lead carbonate and cobalticyanhydric acid. This salt, crystallizing in laminated crystals containing 4 molecules of water, he says, is soluble in about 3 parts of water from which solution it is precipitated by ammonia as a basic salt.

*Mercurous Cobalticyanide*.—Mercurous nitrate gives with potassium cobalticyanide a white, flocculent precipitate, which settles quickly. It was therefore possible to use concentrated ammonia as an indicator. Spot tests on porcelain showed a black precipitate as long as there was an excess of mercurous nitrate. Mercurous cobalticyanide is transposed by hydrochloric acid and seems to be partly changed by hot sulphuric acid but not by oxalic acid. It is unaffected by nitric and acetic acids, but decomposed by alkalies. Mercurous cobalticyanide is probably a normal salt, having the formula,  $\text{Hg}_2\text{Co}(\text{CN})_6$ .

*Mercuric Cobalticyanide* is unknown. There is no precipitate formed when potassium cobalticyanide is added to mercuric chloride either in neutral or acid solution.

*Arsenic*, in hydrochloric, sulphuric, or ammoniacal solution gives no precipitate.

*Antimony* in a solution sufficiently acid to prevent the precipitation of a basic salt, gives no precipitate.

*Stannous* salts in neutral, acid, or potassium hydroxide solution are not precipitated by potassium cobalticyanide. Gmelin<sup>2</sup> states that stannous but not stannic salts are precipitated, but does not give the conditions under which he obtained the precipitation.

*Cupric Cobalticyanide*.—When a solution of copper sulphate is completely precipitated by potassium cobalticyanide solution, there results a turquoise-blue compound. This salt, apparently  $\text{Cu}_2\text{Co}_2(\text{CN})_{12}$ , is insoluble in all acids, cold or hot; very soluble in ammonia, and with caustic potash it turns green, becoming darker and darker until black cupric oxide separates. The ammoniacal solution upon evaporation gives small shining blue crystals to which Zwenger,<sup>3</sup> who first worked with this

<sup>1</sup> *Ann. Chem.* (Liebig), 62, 158.

<sup>2</sup> "Handbook of Chemistry" (1852), Vol. VII, p. 495.

<sup>3</sup> *Loc. cit.*

compound, assigns the formula  $\text{Cu}_2\text{Co}_2(\text{CN})_{12} \cdot 2\text{NH}_3 \cdot 5\text{H}_2\text{O}$ .

*Cuprous Cobalticyanide*, of which no mention is found in the literature, results from the precipitation of cuprous chloride by means of potassium cobalticyanide. It is a faintly yellow precipitate which filters badly; it is insoluble in acids and cold ammonia but soluble in hot, dilute ammonia. It is partly decomposed by potassium hydroxide in the cold and completely when hot. It is slowly oxidized by nitric acid, giving the blue cupric cobalticyanide.

*Bismuth Cobalticyanide*.—A solution of bismuth nitrate, rather strongly acid with nitric acid, is precipitated by potassium cobalticyanide giving a dense white precipitate, very soluble in hydrochloric but insoluble in the other acids and ammonia. Potassium hydroxide gives in the cold  $\text{Bi}(\text{OH})_3$ , which, on boiling, may be changed to yellow  $\text{Bi}_2\text{O}_3$ . The original precipitate seems to be a normal cobalticyanide, but it has not yet been analyzed and no mention of such a compound was found in the literature.

*Cadmium Cobalticyanide*.—The statement appears in Gmelin's "Chemistry" (1852) that with cadmium sulphate, potassium cobalticyanide forms a brown precipitate, turning white later, soluble in excess of cobalticyanide and also in acids. In our experiments cadmium chloride was employed; the precipitate was white and amorphous, not soluble in excess of cobalticyanide nor in any acid except warm hydrochloric acid, from which it reprecipitates on cooling. To determine whether it is changed or not during this treatment will require quantitative work. It is completely soluble in cold ammonia but potassium hydroxide decomposes it, giving cadmium hydroxide.

Solutions of gold, platinum, titanium, vanadium, uranium, or zirconium are not precipitated by potassium cobalticyanide.

Aluminum chloride and chromium salts gave no precipitate with cobalticyanide. Certain double ammonio-chromic cobalticyanides have been described by Christensen<sup>1</sup> and by Braun.<sup>2</sup>

*Ferric Cobalticyanide*.—When potassium cobalticyanide is added to a solution of ferric chloride no precipitate forms at first, but the solution assumes a light green tint and on standing a

<sup>1</sup> *J. prakt. Chem.* [2], 23, 52.

<sup>2</sup> *Ann. Chem.* (Liebig), 125, 153 *et seq.*

few minutes becomes cloudy and iridescent. The precipitation increases with the formation of an amorphous yellow precipitate which runs through the filter. By boiling, it becomes canary-yellow and flocculent, filtering fairly well. The precipitation does not seem to be complete; it is retarded by the presence of an excess of cobalticyanide or by large quantities of ammonium salts. The precipitate once formed is not soluble in cobalticyanide solution, nor in mineral acids, cold or hot, dilute or concentrated. Hydrochloric acid changes the color of the precipitate and renders it almost impossible to filter. Insoluble in acetic acid, cold or hot; when freshly precipitated it is instantly soluble in oxalic acid but reprecipitates on boiling. It seems that at least two different compounds are produced; they differ both in color and solubility; the greenish one is soluble in oxalic acid and the yellow one insoluble. The latter is formed by long standing in the cold or rapidly by heating. Both give ferric hydroxide with ammonia or potassium hydroxide in the cold. If the ferric salt and the cobalticyanide solutions are mixed hot, precipitation of the yellow compound is instantaneous, no matter which reagent is in excess. The well-washed ferric cobalticyanide gives no red color with ammonium thiocyanate.

*Ferrous Cobalticyanide.*—Ferrous sulphate and potassium cobalticyanide seem to give a normal ferrous cobalticyanide,—a slightly yellow, amorphous, slow-settling precipitate. When an excess of cobalticyanide is present there is no oxidation or change of color in the ferrous cobalticyanide, even upon long boiling. The precipitation is complete and filters well. With nitric acid, cold and hot, and with hydrochloric and sulphuric acids, hot, there is oxidation. The precipitate darkens in varying degrees, most with nitric and least with sulphuric acid. After treatment with these acids the precipitate filters badly. No change is noticed with acetic or oxalic acids; in the presence of the latter it filters very well. With ammonia the precipitate is partially decomposed in the cold, becoming bluish, and by boiling is completely converted into ferrous hydroxide. With potassium hydroxide it gives a greenish tint, darkening on standing, becoming slate-colored by boiling, forming probably a mixture of ferrous and ferroso-ferric hydroxides.

*Manganese Cobalticyanide.*—This precipitate, apparently normal, is pure white and filters well. It is insoluble in all cold acids but not absolutely so in hot mineral acids. Alkalies decompose it giving first  $\text{Mn}(\text{OH})_2$ , and later by oxidation,  $\text{Mn}_2\text{O}_3(\text{OH})_2$ .

*Zinc Cobalticyanide* is formed when a solution of zinc sulphate is precipitated by potassium cobalticyanide. It is pure white, settles quickly and filters well; insoluble in hot water, cold or hot acids, except that a trace seems to dissolve in hot sulphuric acid. This precipitate as well as a few others, *e. g.*, ferrous and ferric cobalticyanides, on boiling with hydrochloric acid passes into a condition which renders it impossible to filter even on double filters. It is very soluble in alkalies.

*Cobalt Cobalticyanide.*—From solutions of cobaltous chloride, potassium cobalticyanide precipitates a rose-pink, amorphous, rather gelatinous precipitate which is insoluble in cold and hot acids. At  $100^\circ$  or even lower it loses water and becomes blue. This fact was noted by Zwenger, who also states that he formed this compound by heating cobalticyanhydric acid with concentrated sulphuric acid and diluting with water before the decomposition was complete. A peculiarity of many cobalticyanides is the large amount of water which they retain after drying at  $100^\circ \text{C}$ . Zwenger noticed that the blue anhydrous cobaltous-cobalticyanide rapidly absorbs moisture from the air and that when water is poured upon it, there is a considerable evolution of heat. We found that the ferrocyanides of zinc and manganese acted in the same way. When cobaltous-cobalticyanide is treated cold with ammonia, it gives a brown solution and pink residue; on boiling, the solution becomes pink and the residue greenish-brown. The presence of ammonium salts increases the solubility of this compound in ammonia; it is completely soluble in concentrated ammonia. Caustic potash gives first blue basic salts and on standing or boiling rose-colored cobaltous hydroxide.

*Nickel Cobalticyanide* results when potassium cobalticyanide is added to solutions of nickel salts. Zwenger states that this precipitate cannot be washed free from potassium salts and that the pure nickel cobalticyanide,  $\text{Ni}_2\text{Co}_2(\text{CN})_{12}$ , must be made from cobalticyanhydric acid and a nickel salt. The precipitate is

# SOLUBILITIES OF THE COBALTICYANIDES.

$K_2Co(CN)_6$	(1) $HNO_3$	(2) $HCl$	(3) $H_2SO_4$	(4) $H_2C_2O_4$	(5) $H_2C_2O_4$	(6) $NH_4OH$	(7) $KOH$	Remarks.
+ $AgNO_3$ white, curdy ppt.	(cold) : (hot) :	$AgCl$ $AgCl$	$i$ $i$	$i$ $i$	$i$ $i$	partly s s	$Ag_2O$ $Ag_2O$	Precipitation complete. Settles and filters well. (6) White crystalline ppt (double salt) on evaporation. Easily sol. cold conc. $NH_4OH$ . (3) Seems slightly soluble hot or else is partly changed to $Hg_2SO_4$ . (5) Not changed to oxalate. Filters well. (6) Intense blue solution, giving double $NH_3$ compound on evaporation. (7) Turns green, getting darker until black $CuO$ separates.
+ $Hg_2(NO_3)_2$ wh flocculent ppt.	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$NH_2Hg_2NO_3$ $NH_2Hg_2NO_3$	$Hg_2O$ $Hg_2O$	Precipitation done in strongly acid solution to prevent basic salts upon dilution. (6) Not transposed to $Bi(OH)_3$ . Filters badly. (2) Precipitates again on cooling.
+ $CuSO_4$ turquoise blue ppt.	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$CuO$ $CuO$	
+ $Bi(NO_3)_3$ dense white ppt.	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$Bi(OH)_3$ $Bi_2O_3$	
+ $CdCl_2$ white, amorphous ppt.	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$Cd(OH)_2$ $Cd(OH)_2$	
+ $Fe_2Cl_6$ green, becoming yellow	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$Fe_2(OH)_6$ $Fe_2(OH)_6$	$Fe_2(OH)_6$ $Fe_2(OH)_6$	(5) When freshly precipitated and greenish it is readily sol. in oxalic acid. Ammonia salts in quantity prevent precipitation and excess of $K_2Co(CN)_6$ retards it. (1, 2 and 3) On boiling oxidize more or less to yellow ferric cobalticyanide (6 and 7) Some oxidation to dark-colored ferro-ferric compounds.
+ $FeSO_4$ faintly lowish white p	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	partly $Fe(OH)_2$ $Fe(OH)_2$	$Fe(OH)_2$ $Fe(OH)_2$	
+ $MnCl_2$ white pl	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$Mn(OH)_2$ and $Mn_2O_7(OH)_2$	$Mn(OH)_2$ and $Mn_2O_7(OH)_2$	(1, 2, 3, 4, and 5) Seem very slightly soluble hot.
$ZnSO_4$ dense, white ppt.	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	easily s s	easily s s	(4 and 5) Bump violently on boiling.
+ $CoCl_2$ rose-pink ppt.	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	partly s partly s	$Co(OH)_2$ $Co(OH)_2$	(6) Solubility increased by ammonium salts. Almost completely sol in hot conc $NH_4OH$ . (7) At first blue basic salts, turning again pink. Very voluminous precipitate, which filters poorly.
+ $NiCl_2$ robin's egg blue ppt.	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	$i$ $i$	blue sol. s s	$Ni(OH)_2$ $Ni(OH)_2$	
$NH_4$ , $Li$ , $Na$ , $Mg$ , $Ba$ , $Ca$ , $Sr$ , $Pb$ , $Hg^{II}$ , $Sn^{IV}$ , $C$ , $Al$ , $Pt$ , $Au$ , $Zr$ , $Ti$ , $Mo$ salts.								Solutions of salts of other metals are not precipitated by $K_2Co(CN)_6$ and other known cobalticyanides are easily soluble in water. Such cobalticyanides are usually made from an oxide or hydroxide acted upon by $K_2Co(CN)_6$ .

precipitates.

robin's egg blue in color, very voluminous and dries up to a vitreous mass with conchoidal fracture. It is insoluble in water and acids, cold or hot; soluble completely in ammonia, cold or hot. Potassium hydroxide gives instantly pale green nickel hydroxide.

The effect of the reagents used on the precipitates formed by potassium cobalticyanide is shown by the accompanying table. A glance at this tabulation will show several possibilities for new separations:

1. The lead salt is exceedingly soluble, while those of silver, copper, and bismuth are insoluble in either water or nitric acid. This may find an application in the analysis of pig lead, when the separation of relatively small quantities of these impurities would be much more preferable to the separation of the lead as sulphate. The separation of the bismuth can be effected either by treatment with hydrochloric acid which dissolves the bismuth cobalticyanide and leaves the copper as cobalticyanide and the silver as chloride, or by ammonia which leaves the bismuth and dissolves the copper and silver. The bismuth compound, if not suitable for weighing, can be decomposed by potassium hydroxide and weighed as  $\text{Bi}_2\text{O}_3$ , or one of the new volumetric methods may be employed for its estimation.

2. As the precipitation of ferric cobalticyanide in the cold can be completely prevented by the presence of ammonium sulphate, and probably by other compounds, it is possible to precipitate zinc, manganese, nickel, or cobalt in the presence of iron. With zinc ores containing iron and manganese, the manganese and zinc can be precipitated as cobalticyanides and then separated by treatment with potassium hydroxide, which readily dissolves the zinc cobalticyanide and leaves the manganese as  $\text{Mn}_2\text{O}_3(\text{OH})_2$ .

Another possible application is in the analysis of nickel steel, where the separation from ferric iron, if sufficiently complete, would be more convenient than the method in use, based on the solubility of ferric chloride in ether. The nickel cobalticyanide after filtration can be converted into hydroxide and then dissolved in acid for the cyanide titration or for electrolysis.

These and other possible uses of the cobalticyanides are under investigation at Columbia University.

# SEVENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED IN 1899.

BY F. W. CLARKE.

Received January 15, 1899.

THE year 1899 has not been remarkably prolific in determinations of atomic weight ; and comparatively few investigations have been published. The data are given in the following pages, plus an account of two memoirs which appeared in 1898, but which reached this country only after the report for that year had been printed. These memoirs, by Vandenberghe on molybdenum, and by Kölle on cerium, were issued outside of the usual channels for chemical publication, and so seem to have escaped general notice hitherto.

## BORON.

An elaborate memoir upon the atomic weight of boron has been published by Gautier,<sup>1</sup> who worked upon four different compounds. All weights were reduced to a vacuum, and all calculations were made with the atomic weights recommended a year ago by the committee of the German Chemical Society.

• First, sulphide of boron was decomposed by a dilute solution of caustic soda ; the solution produced was then oxidized by means of bromine water, and the sulphur was precipitated and weighed as barium sulphate. The results obtained were as follows :

Weight $B_2S_3$ .	Weight $BaSO_4$ .	Atomic weight.
0.2754	1.6312	11.032
0.3380	2.0004	11.081
0.3088	1.8300	11.000
0.2637	1.5614	11.050
		Mean, 11.041

The second compound studied was the carbide,  $B_4C$ . This was heated in chlorine gas to eliminate boron ; the residual carbon was then weighed directly, and afterwards burned in oxygen to reweigh as  $CO_2$ . The atomic weights given below were calculated from the weight of the carbon dioxide.

Weight $B_4C$ .	Weight C.	Weight $CO_2$ .	Atomic weight.
0.2686	0.0429	0.1515	11.001
0.3268	0.0512	0.1844	10.994
			Mean, 10.997

<sup>1</sup> *Ann. chim. phys.* (7), 18, 352, November, 1899.



With the third compound, boron tribromide, two series of experiments were made, representing two preparations. The bromide was in each analysis decomposed by water, special precautions being taken to avoid explosive reactions; and the bromine was finally precipitated and weighed as silver bromide. The data are subjoined:

## FIRST SERIES.

Weight BBr <sub>3</sub> .	Weight AgBr.	Atomic weight.
3.1130	6.994	11.009
3.3334	7.490	10.981
3.7456	8.414	11.043
3.2780	7.364	11.032
4.2074	9.452	11.026
		<hr/>
		Mean, 11.018

## SECOND SERIES.

Weight BBr <sub>3</sub> .	Weight AgBr.	Atomic weight.
3.3956	7.628	11.037
4.0295	9.052	11.032
3.7886	8.512	11.003
3.1711	7.124	11.026
		<hr/>
		Mean, 11.025

With boron trichloride the analyses were conducted precisely as in the case of the bromide, silver chloride being the final product weighed.

Weight BCl <sub>3</sub> .	Weight AgCl.	Atomic weight.
2.6412	9.682	10.987
2.7920	10.234	11.000
2.4634	9.026	11.043
3.4489	12.640	11.013
2.2015	8.070	10.992
2.6957	9.878	11.030
		<hr/>
		Mean, 11.011

The mean of the values obtained from the bromide and chloride series, 11.016, is the value which Gautier proposes to adopt.

## NITROGEN.

Dean<sup>1</sup> has continued the investigation which was reported in 1898, relative to the atomic weight of nitrogen. The ratio studied is that between potassium bromide and silver cyanide, and the value finally found is  $N = 14.031$ . Only an abstract of the paper has yet appeared.

<sup>1</sup> *Chem. News*, 80, 279.

## CALCIUM.

A paper upon the atomic weight of calcium, by T. W. Richards, was read at the meeting of the American Association for the Advancement of Science in August, but has not, at the date of this report, been fully published. Five analyses of carefully purified calcium chloride were made to determine the ratio  $\text{CaCl}_2 : 2\text{AgCl}$ . Calculated with  $\text{O} = 16$  and  $\text{Cl} = 35.455$ , the values found for Ca range from 40.121 to 40.130, the mean of all being 40.126.

## NICKEL.

The work of Richards and Cushman upon the atomic weight of nickel, noticed in the report of 1897, has been continued.<sup>1</sup> The sublimed bromide was reduced in hydrogen, giving the ratio between bromine and the metal. The weights corrected for known impurities, and the values found, are as follows :

Weight $\text{NiBr}_2$ .	Weight Ni.	Atomic weight.
2.83325	0.76081	58.705
3.21625	0.86358	58.696
2.31241	0.62094	58.703
2.87953	0.77330	58.710
2.29650	0.61679	58.719
2.98893	0.80272	58.714
5.51291	1.48056	58.716
2.24969	0.60415	58.710
		Mean, 58.709

All weights represent reductions to vacuum, and the antecedent values used in calculation are  $\text{O} = 16$ , and  $\text{Br} = 79.955$ . The complete agreement with the former determinations is almost startling. A full discussion of earlier determinations is given at the close of the paper, and it is shown that the work of Winkler and of Zimmermann is in accord with the new data.

## COBALT.

Just as in the case of nickel, Richards and Baxter have extended their observations upon cobalt,<sup>2</sup> and now give three series of new determinations dependent upon the reduction of bromide to metal. In the first series, which is preliminary, a slight impurity is stated as "residue;" in the other series corrected weights are

<sup>1</sup> *Proc. Amer. Acad.*, 34, 327, February, 1899.

<sup>2</sup> *Ibid.*, 34, 351, February, 1899.

given. The nature of the impurity, however, is fully discussed in the paper.

## FIRST SERIES.

Weight $\text{CoBr}_2$ .	Weight Co.	Residue.	Atomic weight.
5.59216	1.50873	0.00193	59.007
4.61944	1.24807	0.00426	58.996
3.75291	1.01713	0.00793	58.989
3.00645	0.81409	0.00510	59.007
			<hr/>
Mean,			59.000

## SECOND SERIES.

Weight $\text{CoBr}_2$ .	Weight Co.	Atomic weight.
5.32194	1.43428	58.996
7.50786	2.02321	58.989
2.32630	0.62677	58.973
7.44694	2.00736	59.011
		<hr/>
Mean,		58.992

## THIRD SERIES.

Weight $\text{CoBr}_2$ .	Weight Co.	Atomic weight.
5.10891	1.37721	59.016
6.41339	1.72850	58.999
6.59805	1.77876	59.021
3.02854	0.81606	58.982
		<hr/>
Mean,		59.004

The mean of the second and third series is 58.998, when  $\text{O} = 16$  and  $\text{Br} = 79.955$ . Vacuum weights are given throughout.

In a still later paper<sup>1</sup> Richards and Baxter check their determinations of the atomic weight of cobalt by experiments upon the chloride and oxide. The chloride was reduced in hydrogen to metal, and the data obtained, after corrections for known impurities and reduction to a vacuum, were as follows:

Weight $\text{CoCl}_2$ .	Weight Co.	Atomic weight Co.
4.16483	1.89243	59.053
2.30512	1.04723	59.035
		<hr/>
Mean,		59.044

The reduction of cobalt monoxide in hydrogen was similarly effected, but with varying results depending upon differences in the conditions of the experiments.

First, three determinations, with vacuum weights, gave as follows:

<sup>1</sup> *Proc. Amer. Acad.*, 35, 61, August, 1899.

Weight CoO.	Weight Co.	Atomic weight Co.
7.04053	5.53779	58.962
6.69104	5.26312	58.974
7.83211	6.15963	58.927
		<hr/>
		Mean, 58.954

These data, which are not sufficiently concordant among themselves or with the bromide determinations, probably indicate that the cobalt oxide contained some excess of oxygen. In a fourth experiment precautions were taken to avoid this difficulty, and 7.74242 grams of oxide gave 6.09219 of cobalt, whence  $\text{Co} = 59.068$ . In a fifth experiment, resembling the fourth, but with differences in detail, 10.58678 grams of  $\text{CoO}$  gave 8.32611 of metal, corresponding to an atomic weight of  $\text{Co} = 58.929$ .

The authors give elaborate particulars as to the circumstances under which each determination was made, and conclude that cobalt monoxide varies too widely in its composition to be suitable for exact measurements of atomic weight. The true value for cobalt undoubtedly lies between 58.93 and 59.07, the figure 58.995, obtained from the bromide, being the most probable.

#### MOLYBDENUM.

In 1897 the Belgian Academy of Sciences awarded a special Stas prize to M. Ad. Vandenberghe for his determination of the atomic weight of molybdenum. The memoir has recently been published,<sup>1</sup> and the data are now available.

Vandenberghe starts out with molybdenum dibromide, scrupulously purified. From this he obtains metallic molybdenum, by careful reduction in hydrogen at a white heat. The atomic weight determinations are made by the oxidation of  $\text{Mo}$  to  $\text{MoO}_3$ , by means of pure nitric acid. The product was finally dried at a temperature of from  $350^\circ$  to  $400^\circ$ , and cooled in a current of oxygen. The data obtained are as follows:

Weight Mo.	Weight $\text{MoO}_3$ .	Atomic weight.
0.7143	1.0711	95.851
0.3453	0.5177	95.899
0.9693	1.4533	95.889
0.5089	0.7631	95.854
1.7219	2.5820	95.855
<hr/>	<hr/>	<hr/>
4.2597	6.3872	95.869

<sup>1</sup> *Acad. Roy. des Sciences, Mémoires Couronnés*, 4to. series, Tome 56, 1898.

Reducing all weights to a vacuum, the final value becomes 95.829, when  $O = 15.96$ . If  $O = 16$ ,  $Mo = 96.069$ . If  $O = 15.88$ , then  $Mo = 95.349$ . This value is very near that found by Smith and Maas, by an entirely different method, but rather higher than that given by Seubert and Pollard. For all practical purposes the value  $Mo = 96$  may be assumed.

#### TUNGSTEN.

Two investigations relative to the atomic weight of tungsten have been published from the laboratory of the University of Pennsylvania. The first one by G. E. Thomas<sup>1</sup> contains a record of experiments upon  $WO_3$  and  $Na_2WO_4 \cdot 2H_2O$ . The reduction of oxide to metal, and the reverse process of oxidation, gave figures ranging from 183.51 to 184.22 for the atomic weight of tungsten, and work along this line was discontinued. With sodium tungstate three series of dehydration experiments were made, giving the ratio between water and the anhydrous salt as the measure from which to calculate. These results also were discordant, and Thomas discards the method as unsuited to accurate determinations. The object of the paper seems to be negative, and to show that neither method employed is adequate to its purpose.

The second paper, by Professor Smith, contains a section by W. L. Hardin,<sup>2</sup> of similar purport to that of Thomas. Experiments were made upon the oxide, the oxychloride, barium metatungstate, and the precipitation of silver by metallic tungsten, and each method was found to be defective. Discordant results were obtained in each set of trials. The mean of all experiments upon the reduction of  $WO_3$ , and the oxidation of tungsten give approximately the value  $W = 184$ . This value Hardin thinks it best to accept until more conclusive determinations shall have been made.

#### CERIUM.

Kölle's dissertation<sup>3</sup> upon this element deals partly with its atomic weight and partly with other matters. His material was obtained from cerite, and was purified with extreme care. Iodo-

<sup>1</sup> This Journal, 21, 373, April, 1899.

<sup>2</sup> *Ibid.*, 21, 1017, November, 1899.

<sup>3</sup> Beiträge zur Kenntniss des Cers. Doctoral Dissertation by Gotthold Kölle, Zurich, 1898.

metric determinations of cerium salts gave, invariably, results which were too high, and which led him to believe that the source of error was in the accepted atomic weight of cerium, an essential factor in his calculations.

Accordingly, new determinations of atomic weight were made by the standard method; namely, the ignition of cerium sulphate to cerium dioxide. Cerium chloride prepared from the oxide, was spectroscopically examined, and found to be free from other metals. The atomic weight data are as follows, computed with  $O = 16$ .

Weight $Ce_2(SO_4)_3$ .	Weight $CeO_2$ .	Per cent. $CeO_2$ .	Atomic weight.
1.84760	1.11648	60.429	139.11
1.16074	0.70078	60.331	138.78
1.53599	0.92722	60.366	138.73
0.97196	0.58661	60.353	138.64
1.40374	0.84760	60.384	138.84
1.75492	1.05956	60.377	138.80
1.53784	0.92853	60.379	138.82
1.64233	0.99150	60.372	138.76
			Mean, 138.81

This value is lower than any of the later determinations, but agrees nearly with that of Wolf. Like Wolf, and like some other recent investigators, Kölle obtained a white ceric oxide, and he regards the colored preparations of former researches as evidently impure. Furthermore, iodometric estimations made on known quantities of ceric oxide gave good results when the new atomic weight was used in calculation, but excesses of 0.8 per cent. when Brauner's or Robinson's value was employed. So far as present evidence goes there is a presumption in favor of Kölle's determination.

#### PALLADIUM.

Hardin's research<sup>1</sup> upon the atomic weight of palladium is based upon the reduction of certain compounds in hydrogen. Neither of the salts studied had been previously applied to determinations of this character, and the results obtained are therefore of special value. They are, moreover, very concordant, and seem to be more nearly conclusive than any determinations previously made. All weights were reduced to a vacuum, and the

<sup>1</sup> This Journal, 21, 943, November, 1899.

calculations are based upon atomic weights given in the table of your committee for 1898.

First, diphenyl-pallad-diammonium chloride was studied. After reduction, the metal was heated in air to burn off possible free carbon, then reheated in hydrogen, and cooled in air to prevent occlusion of the former gas.

Weight of salt.	Weight Pd.	Atomic weight.
0.98480	0.28953	107.06
1.10000 <sup>*</sup>	0.32310	106.92
1.02820	0.30210	106.96
1.19230	0.35040	107.00
1.40550	0.41300	106.98
1.26000	0.37040	107.04
2.25510	0.66310	107.08
		<hr/>
		Mean, 107.006

The second series of determinations was made upon diphenyl-pallad-diammonium bromide, with the following results :

Weight of salt.	Weight Pd.	Atomic weight.
0.88567	0.20917	107.01
1.31280	0.31000	106.99
1.50465	0.35540	107.03
2.01635	0.47635	107.05
2.92300	0.69080	107.10
		<hr/>
		Mean, 107.036

Finally, ammonium palladium bromide was studied, giving four more determinations.

Weight of salt.	Weight Pd.	Atomic weight.
0.77886	0.18006	107.03
1.53109	0.35381	106.96
2.75168	0.63614	107.03
1.88136	0.43478	106.98
		<hr/>
		Mean, 107.00

The mean of all three series, when  $O = 16$ , is 107.014. 107 then, may be taken, as the most probable value for the atomic weight of palladium.

#### RADIUM.

Madame Curie,<sup>1</sup> having prepared a large quantity of radiferous barium chloride, has determined the chlorine in several fractions

<sup>1</sup> *Chem. News*, 80, 793.

of the material, and so ascertained the atomic weight of the metal contained in it. Three determinations gave for this atomic weight:

140.0  
140.9  
145.8

Hence the atomic weight of radium is higher than that of barium, although its true value is still unknown.

#### THE ELECTROCHEMICAL EQUIVALENTS OF COPPER AND SILVER.

This subject has been reinvestigated somewhat elaborately by Richards, Collins, and Heimrod.<sup>1</sup> First, copper was precipitated in comparison of the silver and copper voltameters, under varying conditions as to temperature, character of solution, and size of plates, and the results are summarized as follows for the atomic weight of copper, when  $\text{Ag} = 107.93$ .

Large plates, cupric solutions, <i>t.</i> 20°,	Cu = 63.47
“ “ “ “ <i>t.</i> 0°,	63.525
Small “ “ “ <i>t.</i> 0°,	63.547
Medium “ cuprous “ <i>t.</i> 0°,	63.573
“ “ “ “ <i>t.</i> 60°,	63.615
Corrected results from cupric solutions,	Cu = 63.563

a value 0.041 lower than that determined by chemical processes.

A study of the silver voltameter by itself showed that it gives results which are too high by about 0.081 per cent. Correcting the atomic weight of copper in accordance with this observation, the true value is found to lie between 63.598 and 63.615. The value previously established by Richards was 63.604, a confirmation of the present work, which is to be continued.

#### TABLE OF ATOMIC WEIGHTS.

In the following table of atomic weights your committee give first its own set of values, based upon both fundamental standards. Next is given Richards' table, revised for 1899, and finally that of the German Chemical Society.<sup>1</sup> The values in the German table are rounded off to convenient approximations for practical use; those of Richards give the nearest significant figure, and the latter policy, which is wise, has also been adopted by your committee. There are, however, slight differences of

<sup>1</sup> *Proc. Amer. Acad.*, 35, 123, December, 1899.



opinion in some cases as to where the nearest significant decimal place really is. Hardin's work on palladium and tungsten, and Kölle's research on cerium, have led to the only notable changes from last year.

	Clarke.		Richards.	German.
	H = 1.	O = 16.		
Aluminum .....	26.9	27.1	27.1	27.1
Antimony .....	119.5	120.4	120.0	120.
Argon .....	?	?	39.9?	40.
Arsenic .....	74.45	75.0	75.0	75.
Barium .....	136.4	137.40	137.43	137.4
Bismuth .....	206.5	208.1	208.0	208.5
Boron .....	10.9	11.0	10.95	11.
Bromine .....	79.34	79.95	79.955	79.96
Cadmium .....	111.55	112.4	112.3	112.
Caesium .....	131.9	132.9	132.9	133.
Calcium .....	39.8	40.1	40.1	40.
Carbon .....	11.9	12.0	12.001	12.00
Cerium .....	138.0	139.0	140.	140.
Chlorine .....	35.18	35.45	35.455	35.45
Chromium .....	51.7	52.1	52.14	52.1
Cobalt .....	58.55	59.00	59.00	59.
Columbium .....	93.0	93.7	94.	94.
Copper .....	63.1	63.6	63.60	63.6
Erbium .....	164.7	166.0	166.	166.
Fluorine .....	18.9	19.05	19.05	19.
Gadolinium .....	155.8	157.0	156.?	....
Gallium .....	69.5	70.0	70.0	70.
Germanium .....	71.9	72.5	72.5	72.
Glucinum .....	9.0	9.1	9.1	9.1
Gold .....	195.7	197.2	197.3	197.2
Helium .....	?	?	4.0?	4.
Hydrogen .....	1.000	1.008	1.0075	1.01
Indium .....	113.1	114.0	114.	114.
Iodine .....	125.89	126.85	126.85	126.85
Iridium .....	191.7	193.1	193.0	193.
Iron .....	55.6	56.0	56.0	56.
Lanthanum .....	137.6	138.6	138.5	138.
Lead .....	205.36	206.92	206.92	206.9
Lithium .....	6.97	7.03	7.03	7.03
Magnesium .....	24.1	24.3	24.36	24.36
Manganese .....	54.6	55.0	55.02	55.
Mercury .....	198.50	200.0	200.0	200.3
Molybdenum .....	95.3	96.0	96.0	96.
Neodymium .....	142.5	143.6	143.6	144.
Nickel .....	58.25	58.70	58.70	58.7

	Clarke.		Richards.	German.
	H = 1.	O = 16.		
Nitrogen .....	13.93,	14.04	14.045	14.04
Osmium .... .	189.6	191.0	190.8	191.
Oxygen .....	15.88	16.000	16.0000	16.00
Palladium.....	106.2	107.0	106.5	106.
Phosphorus .....	30.75	31.0	31.0	31.
Platinum.....	193.4	194.9	195.2	194.8
Potassium .....	38.82	39.11	39.140	39.15
Praseodymium .....	139.4	140.5	140.5	140.
Rhodium.....	102.2	103.0	103.0	103.
Rubidium .....	84.75	85.4	85.44	85.4
Ruthenium .....	100.9	101.7	101.7	101.7
Samarium .....	149.2	150.3	150.0	150.
Scandium .....	43.8	44.1	44.	44.1
Selenium.....	78.6	79.2	79.2	79.1
Silicon .....	28.2	28.4	28.4	28.4
Silver .....	107.11	107.92	107.930	107.93
Sodium.....	22.88	23.05	23.050	23.05
Strontium .....	86.95	87.60	87.68	87.6
Sulphur.....	31.83	32.07	32.065	32.06
Tantalum .....	181.5	182.8	183.	183.
Tellurium.....	126.5	127.5?	127.5?	127.
Terbium .....	158.8	160.	160.	....
Thallium.....	202.61	204.15	204.15	204.1
Thorium .....	230.8	232.6	233.	232.
Thulium .....	169.4	170.7	170.?	....
Tin .....	118.1	119.0	119.0	118.5
Titanium.....	47.8	48.15	48.17	48.1
Tungsten.....	182.6	184.	184.4	184.
Uranium .....	237.8	239.6	240.	239.5
Vanadium.....	51.0	51.4	51.4	51.2
Ytterbium.....	171.9	173.2	173.	173.
Yttrium .....	88.3	89.0	89.0	89.
Zinc .....	64.9	65.4	65.40	65.4
Zirconium .....	89.7	90.4	90.5	90.6

## PRELIMINARY COMMUNICATION ON THE CHEMISTRY OF MUCIN.<sup>1</sup>

BY P. A. LEVENE.

Received December 23, 1899.

THE proteids may be divided into two main groups : First, simple proteids, second, combined proteids. Of the latter the most common are the nucleo-compounds and the mu-

<sup>1</sup> Read before the New York Section of the American Chemical Society, November 10, 1899.

cins. The mucins at present are considered to be compounds of proteids with carbohydrates. This assumption is based on the fact that all the mucins and allied compounds yield, on prolonged treatment with dilute mineral acids, substances reducing Fehling's solution in the same manner as glucose. The true nature of these substances was, however, unknown to the first workers on mucin.

The first successful attempt to obtain a pure carbohydrate was made in Hoppe-Seyler's laboratory. Landwehr stated that he obtained from various mucins a substance very similar in its properties to gum and named it "animal gum." He did not, however, view mucin as consisting of proteid and animal gum, molecularly combined. In his opinion mucins were only a mixture of the two substances. His views on this latter point were subsequently retracted by the author. After Landwehr almost every investigator working on this subject sought for the same "animal gum," and many claimed to have obtained it. Hammarsten succeeded but once in obtaining from mucin a nitrogen-free substance, which, on heating with mineral acids, was capable of reducing an alkaline copper solution. Loebish asserted that by following the conditions indicated by Landwehr he obtained the same "animal gum" from the mucin of fibrous tissue.

A new series of investigations on the entire question of "animal gum" was very recently undertaken by Folin in Hammarsten's laboratory. The latter doubting for certain reasons the correctness of Landwehr's statements, followed as closely as possible all the conditions prescribed by Landwehr, the substances thus obtained never being free from proteid material. Instead of "animal gum" he obtained a "mucinalbumose." Most of the other workers investigated only the composition of the various mucins as such, or the "carbohydrates" resulting from heating the mucins with dilute mineral acids.

There is, however, one property of all the mucins, to which sufficient attention has not been directed. The mucins possess very marked acid properties, more distinct than any simple proteid, and, in fact, more than any carbohydrate, which display no acid character whatever. In explanation of the acid properties two assumptions may be made: First, the substance reducing copper (formed on heating with mineral acids), may be an acid

derivative of some carbohydrate, and secondly, there may be some acid besides the proteid and carbohydrate in the mucin molecule. Loebisch had already noticed that his "animal gum" would decompose carbohydrates, and Hammarsten stated that he could obtain a substance with acid properties from mucins.

The object of this work was to make a thorough study of the acid part of the mucin molecule. My first experiments were made on tendo-mucin obtained according to the method of Chittenden and Gies. The pure mucin was treated for twenty-four to forty-eight hours with a 2 per cent. sodium hydroxide solution and from this solution a substance with acid properties was obtained, by a very simple method, which will be described when the work is completed.

On more detailed examination the substance proved to be nitrogenous. It did not, however, give the biuret reaction, and consequently was free from proteids. On boiling with dilute hydrochloric acid the substance reduced Fehling's solution. The solution of the substance on addition of hydrochloric acid and barium chloride remained perfectly clear, but on boiling yielded a white precipitate. All these properties are peculiar to chondroitin-sulphuric acid. Hence it was natural to assume some relationship between the two substances. Two grams of the substance were heated on a water-bath in 100 cc. of 3 per cent. nitric acid until the solution gave no precipitate with alcohol (this consumed about twenty hours). Several volumes of alcohol and ether were then added to this solution. This yielded only an opalescence; upon addition of a few drops of sodium chloride solution, however, a fine white precipitate formed, which gave the barium test for chondrosin.

The substance gave a precipitate with a solution of Witte's peptone only on addition of acetic acid as long as there was still some of the sodium salt present. When the acid was free from sodium salts, it gave on standing with a neutral albumose solution a flocculent slimy precipitate, resembling genuine mucin. Copper, sodium, and barium salts of the substance were also obtained.

#### ANALYSIS OF THE COPPER SALT.

0.358 gram of the substance was decomposed with hydrochloric acid; the copper was precipitated with hydrogen sulphide and

weighed as  $\text{CuO}$  ; 0.0446 gram  $\text{CuO}$ , or 9.97 per cent. metallic copper was obtained.

Schmiedeberg found the percentage of copper varying between 9.04 and 10.20 per cent. In all these properties, as well as the copper content, this substance resembles chondroitinsulphuric acid.

The next question was whether this ethereal or compound sulphuric acid was only a contamination of the mucin, or constituted an integral part of it. Some of the mucin prepared as above was dissolved in 1 per cent. sodium carbonate, and immediately treated as before for the isolation of the acid ; only traces were, however, obtained. The residue was washed and redissolved and again treated in like manner ; here also only traces were detected. The residue was then thoroughly washed with distilled water until the substance was entirely washed out. The residue was left for twenty-four hours in 200 cc. of 2 per cent. solution of sodium hydroxide. It was then treated as above for the isolation of the substance. The yield was a very good one. I also observed that the acid can be split off from mucin on digesting the latter on the water-bath with addition of a few drops of hydrochloric acid. On digestion with pepsin-hydrochloric acid the mucin also yielded the same acid even after twenty-four hours of digestion. After three weeks of digestion part of the mucin, however, remained undissolved. The investigation into the nature of the residue, as well as of the proteoses thus formed, has so far not been completed.

The next question was whether only the tendo-mucin is a compound of an ethereal sulphuric acid, or whether all the mucins and mucoids have the same composition. The investigation before us thus far embraces only the submaxillary mucin and the substance of a mucoid carcinoma. The submaxillary mucin was obtained by the following method: Freshly removed glands were placed in ether immediately after the death of the animal, and then brought to the laboratory. There they were minced in a chopping machine and allowed to macerate with distilled water for twenty-four hours (large quantities of chloroform being added to keep the tissue from decomposing). The extract was then strained through gauze, well shaken with ether in separatory funnels, and left in the latter for twenty-four hours.

This process caused all the tissue particles and the fat to collect on the surface, the lower layer remaining perfectly clear. It was then filtered and treated for mucin according to the method of Hammarsten. The substance was redissolved and reprecipitated twice. This mucin was treated in the same way as the tendomucin for the ethereal sulphuric acid. But instead of the latter a substance was obtained very similar to that obtained by Folin in Hammarsten's laboratory, and which he called mucinalbumose.

After several futile attempts to obtain the acid free from proteids I finally obtained positive results by the following method: The mucin was digested for one hour in a Koch sterilizer with 0.1 per cent. hydrochloric acid solution. The solution, being then neutralized with sodium hydroxide, was treated with large quantities of alcohol. The precipitates thus formed were treated with 5 per cent. sodium hydroxide and allowed to stand over night. This solution was treated in two different ways, each yielding positive results: (1) The solution was treated with Brucke's reagent and hydrochloric acid. The filtrate did not give any precipitate on addition of alcohol and ether. If, however, a sufficient quantity of sodium hydroxide was added previously to the alcohol to render the solution slightly alkaline, a yellowish precipitate was formed very similar to that of the sodium salt of the ethereal sulphuric acid. The precipitate was redissolved in dilute sodium hydroxide solution, filtered and reprecipitated with alcohol. The substance thus obtained precipitated an acid solution of albumose, reduced Fehling's solution on boiling with hydrochloric acid, and on addition of hydrochloric acid and barium chloride gave a precipitate only upon heating. It was nitrogenous and did not give the biuret reaction. There was not enough of the substance to attempt the chondrosin test.

In another experiment phosphotungstic acid was used instead of Brucke's reagent. The result was the same.

From this may be concluded that the submaxillary mucin contains in its molecule a substance which is either chondroitin-sulphuric acid or closely related to it. The investigation of a mucoid carcinoma by the same method as the submaxillary mucin revealed the presence of a similar substance. The study

of ovomucoid, mucoid of the thyroid gland and of a mucoid tumor is now in progress.

I was prompted to make the present communication by the fact that about ten days ago an article appeared in Hoppe-Seyler's *Zeitschrift*. The author analyzed an ovarian mucoid and found a substance similar to chondroitinsulphuric acid. His findings on the latter mucoid coincide with mine on several mucins and justify the conclusions I was ready to draw from my work, that mucins are not simple compounds of proteids and carbohydrates, but are proteid derivatives of an ethereal sulphuric acid.

I consider it premature at this moment to state positively the nature of this combination.

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### THE DETERMINATION OF GLYCOGEN AND RELATIVE QUANTITIES OF GLYCOGEN IN DIFFERENT PARTS OF THE FLESH OF A HORSE.

BY J. K. HAYWOOD.

Received January 16, 1900.

A GREAT many methods have been proposed for the estimation of glycogen,<sup>1</sup> but on trying them I found that nearly all were open to some serious objection, which rendered their employment either entirely out of the question or the results obtained very doubtful. I have, therefore, worked out a method which, although not new in principle, is new in many of the details which go to making up a fairly accurate and speedy procedure. But first I will speak of some of my preliminary experiments to show future workers in this field, at least, what *not to do*.

<sup>1</sup> Wiley's "Principles and Practice of Agricultural Analysis", 3, 554.

Having seen in a paper by Von Wittich<sup>1</sup> that glycogen might be determined by digesting the sample of meat on the steam-bath for two or three hours, with water containing a few drops of sulphuric acid, filtering, neutralizing, filtering again, determining the reducing sugar in the filtrate by Fehling solution, and from that figure calculating the glycogen, I thought I would try this, as it seemed the easiest way. I added, however, more than a few drops of sulphuric acid,—in fact, made a 3 per cent. solution; for it is well known that glycogen is more resistant to the action of acids than starch, and a few drops of sulphuric acid would not convert starch in this time. I also continued the digestion for six hours. I encountered a difficulty at once; *i. e.*, the mixture would not filter after digestion, except very slowly,—so slowly that a practical use of the method was impossible. I therefore neutralized immediately after digestion, made to a volume, and filtered off an aliquot portion, which still took a long enough time, but was much shorter than filtering the whole. Using a dried, ether-extracted liver, I obtained results of 1.27 and 1.29 per cent. glycogen, which looked encouraging from the closeness of the duplicates. The Fehling solution filtrate, however, looked dirty, and the copper suboxide precipitated was not red, but a dirty green, such as no chemist likes to see.

I therefore carried through a sample of the liver, using the above method, except that at the end the solution was clarified with lead subacetate, the excess of lead removed by sodium sulphate, and the dextrose determined in the filtrate. In this way a clear Fehling filtrate was obtained, but the results did not at all compare either with each other or with those (1.29 and 1.27) mentioned above. In one case I obtained a result of 0.87 per cent. glycogen, and in a duplicate 0.00 per cent. glycogen.

Thinking from the work of Külz and Bornträger<sup>2</sup> that hydrochloric acid might be a better agent to convert the glycogen to dextrose, I next boiled some of the liver for three hours with 200 cc. of water and 20 cc. of hydrochloric acid (sp. gr. 1.125), neutralized with sodium carbonate, and filtered just as in the determination of starch. The result on a non-clarified portion was 4.72 per cent. glycogen, and on a portion clarified by lead

<sup>1</sup> *Central-Blatt. f. d. med. Wissenschaft*, 13, 292 (1875).

<sup>2</sup> *Archiv. f. d. ges. Physiologie*, 24, 28.



subacetate, and the excess of lead removed by sodium sulphate, the result was 1.25 per cent. glycogen. I again determined the glycogen as above, except that the solution at the end was clarified with neutral lead acetate, and results of only 0.03 and 0.04 per cent. glycogen were obtained.

I next added 1 per cent. of starch to a sample of meat which gave no glycogen by the above method, and 1 per cent. of glycogen to another portion of the same meat. The samples thus prepared were treated just as in the determination of starch, and at the end clarified with neutral lead acetate, and the excess of lead removed. Proceeding in this way I could only recover 0.08 per cent. starch and 0.00 per cent. glycogen.

With results thus varying in the case of a sample of liver from 0.00 per cent. to 4.72 per cent., and results of 0.00 per cent. and 0.08 per cent., where 1 per cent. of glycogen and 1 per cent. of starch respectively had been added, it appeared that the method was absolutely worthless; so it was abandoned.

It may seem strange, at first sight, that no better results than the above could be obtained following after Külz & Bornträger<sup>1</sup> who had worked out a method based on the inversion of glycogen to dextrose and the determination of the latter by Fehling solution; but this apparent contradiction will disappear when I call attention to the fact that Külz only worked on *pure* glycogen, and in no case mixed his glycogen with meat and recovered it.

I did not make an attempt to estimate glycogen by means of the polariscope, as also given by Külz,<sup>2</sup> because Külz had worked with rather large quantities, so that if only 0.00 to 1.5 per cent. of glycogen were present the determination would be very uncertain, since if a workable quantity of the meat were used (say 50 to 60 grams), the reading on the sugar scale would be only a few tenths of a degree.

Estimating glycogen by the depth of its color with iodine, according to Goldstein,<sup>3</sup> was not employed, as it has been shown to be worthless by many subsequent investigators.

A qualitative test for glycogen by the test of Bräutigam and

<sup>1</sup> *Archiv. f. d. ges. Physiologie*, 24, 28.

<sup>2</sup> *Ibid.*, 24, 87 and 24, 90.

<sup>3</sup> *Verhandlungen der physik-med. Gesell. in Würzburg*, 7, 1.

Edelmann,<sup>1</sup> by means of iodine, was not employed, because subsequent investigators have been able to obtain the same test with other meats besides horse meat, notably on beef.

I therefore decided to try the method of Brücke,<sup>2</sup> which appeared to promise better results than any of the other gravimetric methods. Brücke digests the meat on the steam-bath with water, filters, precipitates the proteid matter in hydrochloric acid solution with the double iodide of potassium and mercury, again filters, precipitates the glycogen in the filtrate with alcohol, filters on a weighed filter, washes first with 60 per cent. alcohol, then with 95 per cent. alcohol, then with ether, dries at 115° C., and weighs. This method has been examined by many later investigators. Külz<sup>3</sup> found that an extraction of the meat with water was not sufficient, but that it was better to employ a weak solution of potassium hydroxide. Kratschmer<sup>4</sup> found that the hydrochloric acid of the Brücke reagent acted on the freshly precipitated glycogen; also that it was best to first dry the glycogen at 80°–100° C., and then at 115°. I took all of these points into consideration when working out the method.

But first of all a serious difficulty was met with. It was found impossible to filter the meat digested with potassium hydroxide in a reasonable length of time, and nearly impossible to get off any fair-sized aliquot portion. Instead of filtering after the digestion with a weak solution of potassium hydroxide, the mixture was made immediately acid with hydrochloric acid, in the presence of the unattacked residue, Brücke's reagent added to precipitate proteid matter, the whole made to a volume, and an aliquot portion filtered off. In this way a very easily filterable mass was obtained. After an aliquot portion, say 250 cc. out of 500 cc., had been thus obtained, it was neutralized with a solution of potassium hydroxide (using a drop of phenolphthalein as indicator, and noting the amount of hydroxide employed) to get rid of the hydrochloric acid, which would, according to Kratschmer, act on the glycogen. When exact neutralization had been obtained, small flakes of some non-glycogen material would usually separate out. These were filtered

<sup>1</sup> *Ztschr. anal. Chem.*, 33, 98.

<sup>2</sup> *Central-Blatt f. d. med. Wissenschaft*, 1871, 388.

<sup>3</sup> *Ztschr. für Biologie*, 22, 161.

<sup>4</sup> *Archiv. f. d. ges. Physiologie*, 24, 134.

off, a few drops of hydrochloric acid added to the filtrate, and twice the volume of 92 to 95 per cent. alcohol added. The precipitated glycogen was, at the end of a few hours, filtered off through a weighed filter, washed first with 60 per cent. alcohol, then with 95 per cent. alcohol, then with ether, dried at 80°-100° C., then at 115° C. and weighed again, the gain representing glycogen. In this way a result of 0.51 per cent. was obtained on a dry roast beef, and where 0.87 per cent. and 1.61 per cent. glycogen were added, 0.82 per cent. and 1.54 per cent. respectively were recovered. In each of the above determinations, however, something seemed to come down besides the glycogen, and on treating the filter with hot water this would mostly remain as a residue, and the glycogen be dissolved. It appeared from this, then, that a much better method than the one above was to weigh the filter and contents after drying, then dissolve out glycogen with water, dry and weigh again, and thus determine glycogen by the difference in weight. To test this I carried through a sample of roast beef, and on the water-free, fat-free sample by first method obtained a result of 0.3 per cent. glycogen; by second, 0.17 per cent. glycogen; on a liver I obtained 1.53, 1.56 per cent. by the first, and by second, 1.04, 1.10 per cent.; on a chicken I obtained 0.35 per cent. by the first, and by the second 0.26 per cent. It would therefore appear that all of the proteid matter was not precipitated by the double iodide of potassium and mercury, but that some which was nearly entirely insoluble in water came down with the glycogen and remained on the filter when the glycogen was dissolved.

From all of the above work I have settled upon the following method for determining glycogen. From 50 to 60 grams of meat, after having been run through a sausage grinder, is treated in an evaporating dish with 300 cc. of a 1 per cent. potassium hydroxide solution, and heated on the steam-bath for about six hours, water being added from time to time, so that the volume never becomes less than 150 cc. Finally the water is removed by evaporation until about 150 cc. remain. This is made slightly acid with hydrochloric acid (1-5), and hydrochloric acid and double iodide of potassium and mercury<sup>1</sup> added alternately until all pro-

<sup>1</sup> The double iodide of potassium and mercury is prepared by first precipitating a solution of mercuric chloride with potassium iodide, washing the precipitated mercuric iodide till free of chlorides, then saturating a 10 per cent. potassium iodide solution with the mercuric iodide at the boiling temperature.

teid matter is precipitated. The hydrochloric acid is added about 2 cc. at a time, and the double iodide of potassium and mercury about 10 cc. at a time. Usually about 20-25 cc. acid (1-5) and 70-100 cc. of the iodide solution are required. When the proteid matter separates, and leaves a clear liquid layer above, a small amount of this is carefully poured off and tested for complete precipitation. If the precipitation is not complete the liquid is returned, and the proteid precipitant added until the clear liquid above the proteid matter gives no precipitate with hydrochloric acid and the double iodide solution. Sometimes, not often, the proteid matter will not separate. In this case follow Külz's method of nearly neutralizing with potassium hydroxide and adding again hydrochloric acid, and the precipitate will usually flocculate. The proteid matter being now precipitated as completely as possible, the whole is transferred to a 500 cc. flask, made to the mark with water, well shaken, and an aliquot portion (say 250 cc.) filtered through a fluted filter. A drop or two of phenol phthalein is now added, and the solution titrated to exact neutrality with a concentrated solution of potassium hydroxide, noting the amount used. If a slight amount of flakey-looking matter separates at this point, the liquid is again passed through a fluted filter, and such a volume taken as will correspond to  $\frac{2}{5}$  of the original material, of course taking into consideration the number of cubic centimeters of potassium hydroxide used to neutralize the hydrochloric acid. Three or four drops of concentrated hydrochloric acid are now added, and twice the volume of from 93 to 95 per cent. alcohol. After standing two or three hours the precipitated glycogen is filtered off through a paper filter, washed with 60 per cent. alcohol, then with 95 per cent. alcohol, then with ether; dried at  $80^{\circ}$ - $100^{\circ}$  C., then at  $115^{\circ}$  C., and weighed in a weighing tube. The filter is then extracted thoroughly with boiling water, dried again at  $115^{\circ}$  C., and again weighed in a weighing tube, the difference in weight representing glycogen.

Proceeding in this way, I obtained on roast beef 0.17 per cent. glycogen, calculated to the dry, fat-free basis; where 0.87 per cent. glycogen was added, 0.78 per cent. was recovered; and where 1.72 per cent. glycogen was added, 1.57 per cent. was

recovered. Close duplicates were also obtained by this method, as shown from the following work :

On a liver the results were 1.04 and 1.10 per cent. calculated to dry, fat-free basis.

On a chicken the results were 0.26 and 0.29 per cent. calculated to dry, fat-free basis.

On an ox tongue the results were 0.27 and 0.30 per cent. calculated to dry, fat-free basis.

On another ox tongue the results were 0.65 and 0.62 per cent. calculated to dry, fat-free basis.

Following will be found the analysis of three parts of three different horses, the glycogen of which was determined by the above method. First I will mention, however, that in addition to the direct determination of glycogen I also estimated the reducing sugars in a water extract of each sample of meat, as suggested by Niebel<sup>1</sup> to find the amount of glycogen that had been converted to dextrose. This was done by boiling the meat three separate times with 500 cc. portions of water, pouring off the water each time, evaporating to a small volume, clarifying with neutral lead acetate, removing excess of lead with sodium carbonate, making to a volume, filtering off an aliquot portion, and determining the dextrose in the filtrate by Allihn's method.

No. of sample.	Part of horse.	Water.	Fat.	Glycogen.	Glycogen correspond- ing to dextrose.	Glycogen in each of the preceding col- umns calculated to fat-free, water-free basis.	
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	chuck	70.57	9.01	0.30	0.00	1.47	0.00
2	chuck	74.30	4.63	0.48	0.00	2.28	0.00
3	chuck	77.22	5.84	0.86	0.00	5.08	0.00
4	rib	66.12	12.51	0.61	0.00	2.85	0.00
5	rib	72.87	4.54	0.54	0.00	2.39	0.00
6	rib	76.31	1.24	0.79	0.00	3.52	0.00
7	flank	57.93	25.01	0.42	0.00	2.46	0.00
8	flank	71.79	7.66	0.33	0.00	1.61	0.00
9	flank	76.39	1.16	0.53	0.00	2.36	0.00

In four of the above samples a determination was made of the amount of nitrogen in the glycogen dissolved from the filter, to

<sup>1</sup> *Ztschr. f. Fleisch. u. Milch. Hygiene*, 1, 185, 210, and 5, 86, 130.

see how much, if any, proteid matter had not been removed, but still contaminated the glycogen. In four more of the above samples a determination was made of the amount of ash in the glycogen to see if a correction was necessary. The results are given below.

No. of sample.	Amount of original beef used. Grams.	Amount of beef used in actual determination, being 2/5 of original. Grams.	Amount of glycogen found. Grams.	Amount of proteid matter $6.25 \times N$ . Grams.	Amount of ash. Grams.
1	60	24	0.0717	0.0009	....
2	60	24	0.1148	....	0.0048
3	60	24	0.2070	....	0.0065
4	60	24	0.1467	0.0018	....
5	60	24	0.1304	0.0017	....
6	60	24	0.1898	0.0024	....
7	60	24	0.0999	....	0.0030
9	60	24	0.1282	....	0.0025

It will thus be seen that only a small percentage of the glycogen consists of proteid matter and ash, and when these two are added together, and calculated back as per cent. of the original substance, the figure for glycogen will only be altered by about 0.02 per cent.

In several other determinations of glycogen, the glycogen which was dissolved from the filter was evaporated to a small volume and tested with Brücke reagent and with bromine, to see if any proteid matter was precipitated. In no case did any come down.

From this work it will be seen that the glycogen obtained is quite pure, only a small portion consisting of ash and proteid matter. The small plus error caused by these substances, in all probability, about balances the negative error caused by the action of hydrochloric acid on the glycogen during the precipitation of proteid matter.

While the above method is, I think, much more accurate than the original Brücke method, it does not possess the accuracy of a chlorine or sulphuric acid determination, but this is not necessary, since the end of the work is not to know the amount of glycogen to 0.01 per cent., but to distinguish horse meat from other meats by its high content of glycogen.

Appended will be found analyses of several parts of a single horse. These are not given to show anything about the accuracy of the method, but to increase the data relating to the amount of glycogen in different cuts of horse meat. The horse was one which had been killed in an accident, three days before the analysis was made.

No. of sample.	Part of horse.	Water.	Fat.	Glycogen.	Glycogen corre- sponding to dex- trose.	Glycogen in each of the preceding columns, calcu- lated to fat-free, water-free basis.	
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
1	Second cut of round..	74.36	3.27	0.49	0.00	2.19	0.00
2	First cut of round....	73.77	3.23	0.27	0.05	1.17	0.22
3	Shoulder clod.....	73.54	5.27	0.58	0.05	2.73	0.23
4	Cross ribs.....	73.86	6.30	0.32	0.04	1.62	0.20
5	Chuck.....	68.00	15.39	0.34	0.00	2.05	0.00
6	Plate .....	52.16	33.66	0.41	0.00	2.89	0.00
7	Brisket .....	66.70	12.16	0.46	0.006	2.17	0.03

I would like to express my thanks to Dr. W. D. Bigelow, of this Division, for putting at my disposal a very complete bibliography of glycogen. Since his work will shortly appear in print, I will not attempt to go into the literature of the subject.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 15.]

THE ELECTROLYTIC DEPOSITION OF BRASS.

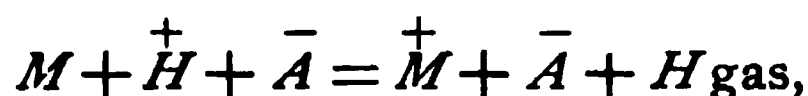
BY J. LIVINGSTON R. MORGAN.

Received January 19, 1900.

BRASS plating by electrolysis was discovered in 1841, and the original process, with a few modifications, is still in use at the present time. The formulas for the preparation of the bath are entirely empirical, the subject, so far as I know, having never been treated from the theoretical standpoint. The purpose of this paper is to consider the reaction by the light of our present knowledge of electrochemistry, and to present the theory of the process which results.

When a metal with a high electrolytic solution pressure (Zn) is placed in an acid solution and connected by a wire to a plate of platinum, immersed in the same liquid, hydrogen gas is

given off, at the platinum side, in the form of bubbles. The chemical reaction is



where  $M$  represents a monovalent metal, and  $HA$  a monobasic acid, which is dissociated into the ions  $\overset{+}{H}$  and  $\bar{A}$ . The process consists, essentially, in, the formation of metallic ions, which force ions of hydrogen out of the solution. A certain difference of potential results from this reaction which may be calculated by aid of the formula

$$\pi = \frac{0.0002}{n} T \log. \frac{P}{p} - 0.0002 T \log. \frac{P_1}{p_1} \text{ volts,}$$

where  $n$  is the valence of the metal,  $P$  its electrolytic solution pressure, and  $p$  the osmotic counter pressure of the metallic ions in solution, while  $P_1$  and  $p_1$  are the corresponding figures for hydrogen. The end of such a reaction will be reached, of course, when the solution is saturated with ions of the metal; *i. e.*, when all ions of hydrogen have disappeared.

When a metal possessing a low electrolytic solution pressure (Cu) is placed in acid, no hydrogen gas is given off, and ions of this metal in a solution would precipitate in the metallic form upon the plate.

When the metal plate in the above arrangement is used as the anode of a decomposition cell the general action of a metal with a high electrolytic solution pressure is the same, only intensified. With a metal of low electrolytic solution pressure the action is reversed so that if the electromotive force is made sufficiently high the metal acts as one of the former class and separates hydrogen from the acid. The value of the term  $P$  then can always be increased by an external electromotive force. Thus by reversing a Daniell cell and sending a current from the copper to the zinc, through the liquid, copper is dissolved and zinc precipitated. If a solution of a copper salt is electrolyzed with a copper anode, the value of  $P$  is increased until it exceeds the value  $p$ ; *i. e.*, the osmotic counter pressure of the copper ions. At the cathode the copper ions accumulate, and are forced out of a solution upon the plate. With copper this would naturally take



place even without a great accumulation of ions, but with a metal of high electrolytic solution pressure the ions would separate only when the term  $p$  is made greater than  $P$ . The work necessary for plating with a metal of high electrolytic solution pressure is thus seen to be done at the cathode, for there  $P$  must be exceeded by  $p$ , while for one with a low electrolytic solution pressure it is done at the anode for there it is necessary for  $P$  to exceed  $p$  in value. In other words metals like zinc, in simple solutions, need the current to separate them from the solution, while those like copper need it to cause the anode to dissolve. If the decomposing electromotive force is great enough, hydrogen will also be separated at the cathode, for ions of hydrogen will accumulate then and be evolved as gas when the electromotive force causes  $p$ , to exceed  $P$ , in value. With a small electromotive force, however, this will not take place so that for our purposes we may leave it out of consideration entirely.

If an alloy, made up of two metals one of which has a very high electrolytic solution pressure, while the other has a very low one, is placed in acid the constituent with the high pressure will dissolve, separating hydrogen gas upon a platinum plate, while the other will be unaffected. The end of the reaction will be reached when the acid is saturated with the ions of the one metal or if there is an excess of acid, when the one metal is entirely dissolved. Using such an alloy as the anode of a decomposition cell, both constituents will go into solution. The amounts dissolved will be proportional to the values of the electrolytic solution pressure. If the electrolyte in the cell contains ions of each constituent, then at any one decomposing electromotive force the amounts dissolved will be proportional to the electrolytic solution pressures divided by the osmotic counter pressures of the metallic ions. If the alloy contains 50 per cent. of each constituent it will be necessary for its solution in unchanged ratio, that

$\frac{P}{p} = \frac{P'}{p'}$ , where  $P$  and  $P'$  are the electrolytic solution pressures of the two metals and  $p$  and  $p'$  the osmotic pressures of their ions. In other words it is necessary that the ionic concentration of the metals be proportional to the electrolytic solution pressures. This relation is shown most plainly by the following diagram :

$$\left. \begin{array}{c} \text{Cu} \\ \text{Zn} \end{array} \right\} 50 \text{ per cent.} \left[ \begin{array}{l} \rightarrow P_{\text{Cu}} = 4.8 \times 10^{-20} \text{ At.} \\ \leftarrow p_{\text{Cu}} = 4.8 \times 10^{-20} \text{ At.} \\ \leftarrow p_{\text{Zn}} = 9.9 \times 10^{+18} \text{ At.} \\ \rightarrow P_{\text{Zn}} = 9.9 \times 10^{+18} \text{ At.} \end{array} \right]$$

The two opposing pressures, osmotic and electrolytic solution, are thus equalized for each of the two metals; hence an electromotive force applied to the alloy as anode will cause equal amounts of copper and zinc to be dissolved. Such a mixture would be made if a saturated solution of a zinc salt were in contact with a plate of the 50 per cent. alloy, and the alloy, when made the anode, would dissolve evenly. It is necessary now, however, to consider the cathode upon which the metal will be precipitated. Here we will not get, at any current density, the alloy we expect so that the relation between the zinc and copper ions in the solution will change, and consequently the two constituents will then be dissolved from the anode in another ratio. *For the deposition of any alloy, then, we see that it is necessary that the following conditions be fulfilled: 1. That the solution have such an ionic concentration of the two metals that the correct amount of each constituent dissolves from the anode; i. e., that the alloy dissolves as such. 2. That the correct alloy separates at the cathode, so that the composition of the liquid is not altered in such a way that the first condition is unfulfilled.* With alloys of copper and zinc we see that, for simple salt solutions, the first condition can be fulfilled, but the second can not.

A solution from which brass may be deposited and which will retain this power, by dissolving the correct proportions of copper and zinc from the anode, must have the following properties, which are self-evident from what has already been said: *1. It must contain ions of zinc and copper in such a proportion that 30 per cent. of zinc, and 70 per cent. of copper will be dissolved from the anode; i. e.,  $\frac{P}{p} : \frac{P'}{p'} :: 30 : 70$ . 2. It must contain complex ions of zinc and copper, from which these metals may be separated.* These are necessary, for we have seen that simple metallic ions cause changes in the composition of the solution and thus vary the composition of the alloy dissolved. There is also less work needed to separate metals from complex ions than from simple ones. *3. For economy, the maximum concentration of copper*

*ions should be as small as possible in order that copper may be separated easily from the anode.*

All these conditions are fulfilled by a solution of the mixed salts of copper and zinc in potassium cyanide solution. We have first an extremely small concentration of zinc and copper ions. The absolute value of the concentration of copper ions can be appreciated from the consideration of the following experiment: When a solution of potassium cyanide is poured upon the copper side of a Daniell cell, the poles are reversed; *i. e.*, copper becomes the negative pole. In order to do this, it is necessary that

$$\frac{P}{p} (\text{ZnSO}_4) < \frac{P'}{p'} (\text{CuSO}_4 \text{ in KCN});$$

*i. e.*, that the value of  $p$  becomes so small that  $P' (= 4.8 \times 10^{-20})$  exceeds it and copper goes into solution. We have the complex ions  $\text{Zn}(\text{CN})_4^-$  and  $\text{Cu}(\text{CN})_4^-$ , from which zinc and copper may be deposited in varying proportions according to the current density, for zinc needs a greater current density than copper. In other words from our theoretical knowledge we can predict that such a solution would serve our purpose.

It would seem necessary, next, to find just what proportion of zinc and copper salt should be present in the cyanide solution, to give the correct ratio of ions. This, however, is not necessary, as is shown by the following consideration, for this ratio adjusts itself automatically during the reaction. In practice, at times, a bath is made up as follows: A solution of potassium cyanide is electrolyzed, at the correct density to deposit brass, for several hours with brass electrodes, the liquid being drawn off and used as the bath. From the brass anode ions of zinc and copper ions are given off into the solution forming the salts  $\text{K}_2\text{ZnCN}_4$  and  $\text{K}_2\text{CuCN}_4$ . These salts dissociate, to a very large extent, into  $2\text{K}^+$  and  $\text{MCN}_4^-$ , where  $M$  represents either copper or zinc. There is also a further dissociation, to a very slight degree, into  $2\text{K}^+$ ,  $\text{M}^{++}$  and  $4\text{CN}^-$ . The zinc, on account of its high electrolytic solution pressure, will dissolve to a greater extent than the copper, so that there will be more ions of  $\text{ZnCN}_4^-$  than of  $\text{CuCN}_4^-$ . Only 30 parts of zinc, however, at this current density can separate to

every 70 parts of copper so that there is also a concentration of  $\text{ZnCN}_4^{--}$  ions on the cathode side; this takes place after hydrogen has been given off for a time. The equilibrium in the solution is fixed by certain equations. By these only a certain amount of free zinc ions can exist in the solution, all over this amount being transformed into  $\text{ZnCN}_4^{--}$ , and of this latter a relatively small portion only can separate at the cathode. For this reason when the solution becomes saturated with  $\text{ZnCN}_4^{--}$  ions, it exerts the same counter pressure with its free zinc ions as it would if the solution were saturated with zinc ions, since any more zinc ions would supersaturate the solution. For this reason zinc can only dissolve to the same amount in which it separates.

The copper ions in the solution are so few that, as before observed, the metal acts as though it possessed a high electrolytic solution pressure. There is a larger number of  $\text{CuCN}_4^{--}$  ions and since these break up and separate copper to a greater extent than those of  $\text{ZnCN}_4^{--}$  separate zinc, and since the solution never becomes saturated with them, the terms  $\frac{P}{p}$  and  $\frac{P'}{p'}$  become of the same order, and are related as 30 : 70. It is thus seen that the regulation of the relative concentration of zinc and copper dissolved is automatic and depends upon the current density which regulates the ratio deposited. In few words we may sum up the behavior as follows: The solution is saturated with zinc, since no more can exist either as Zn or as  $\text{ZnCN}_4^{--}$ , except as Zn from  $\text{ZnCN}_4^{--}$  separates. The relation  $\frac{P'}{p'}$  is increased by the exceedingly small value of  $p'$  so that ions of copper can form, but as they form they separate on the other side, removing the saturated condition with respect to zinc, so that the correct relative amount of this also can separate and dissolve, etc.

Another method consists in dissolving equal weights of copper and zinc salts in a solution of potassium cyanide. The action, of course, is exactly similar to that given above for potassium cyanide solution alone, so that it will not be necessary for us to consider it.

It is thus possible from purely theoretical knowledge, and a few appropriate simple experiments to find just what solutions must be used for baths for the deposition of any alloy. The contrast between this method and the old empirical one of trying all combinations until a lucky hit is made, the true reasons for which are unknown, is striking, but it is just what is being experienced to-day in all branches of chemistry by the application of theory to practice. The other ingredients which are used in the baths are to produce a fine smooth coating and have nothing to do with the theory of the method. Of course there are other solutions which behave just as the double cyanides do, but as the theory is the same, the only idea of a change would be for economy and that is a question for the technical side of the subject. Such another solution which is used is made by dissolving zinc and copper salts in an excess of ammonia. Here we have just as before  $\text{Zn}$  and  $\text{Cu}$  ions, and also complex ones which behave just as  $\text{CuCN}_2$  and  $\text{ZnCN}_2$ .

Another liquid which causes copper to act as a metal of high electrolytic solution pressure is a solution of potassium sulphide.

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## THE DETERMINATION OF SULPHUR IN BITUMENS.

BY A. C. LANGMUIR.

Received November 24, 1899.

IN the September number of this Journal, S. F. and H. E. Peckham criticize a paper by E. H. Hodgson which appeared in November, 1898, and describe, in some detail, their own method slightly modified.

The authors claim for their method that it is "simple, reasonably rapid and accurate" and state that it is "susceptible of great accuracy, if *conducted with care*. It requires great care from the beginning to the end. Mr. Hodgson's results do not indicate great care,—they are not sufficiently concordant."

It is but fair to Mr. Hodgson to call attention to certain features in Messrs. Peckham's method which cannot inspire chemists with confidence and which may possibly indicate that the authors themselves have not bestowed on their method the great care which they miss in Mr. Hodgson's work.

A brief review of the method is necessary: Approximately

0.5 gram of the bitumen is fused with 30 grams of a mixture of equal parts of sodium carbonate and potassium nitrate in a platinum crucible. The crucible contents are dissolved in water, hydrochloric acid is added, and the silica is separated by evaporation on the water-bath and dehydration. After taking up with hydrochloric acid and water the silica is filtered and the filtrate is rendered alkaline with ammonia to precipitate iron and alumina. The excess of ammonia is removed by boiling, and the iron and aluminum are filtered off. The lime is removed by ammonium oxalate and in the filtrate from the latter, now free from silica, alumina, iron and lime, the sulphuric acid is precipitated by the usual method. The convenience of estimating the mineral constituents in the same solution with the sulphuric acid is noted. In our opinion, what is gained in convenience, if any, by this method, is lost in accuracy.

In some bitumens the amount of sulphur is very low. In others the proportion of mineral matter is so high that very considerable amounts of iron, alumina, or lime may be met in the course of the analysis.

If the above method is to be generally applied the following objections should first be answered:

In the course of the fusion with alkaline carbonate and nitrate there is danger of the absorption of sulphuric acid produced by the burning gas. Any error from this cause would be especially noticed in the analysis of bitumens low in sulphur. An alcohol lamp should be used or the crucible should rest in a hole cut in asbestos board to protect the fusion from the access of the products of combustion.

Messrs. Peckham have not given us details sufficient to enable us to decide whether they have made use of these necessary precautions. Several chemists have called attention to this danger.<sup>1</sup>

In the slow evaporation of the fusion on the water-bath there is again a possible source of error in the absorption of sulphur, if, as is often the case, the bath is heated by gas.

Hillebrand<sup>2</sup> finds that the sulphur introduced in this way in the analysis of silicate rocks is frequently as much as the entire sulphur present. The writer's own experience has confirmed

<sup>1</sup> Price : *J. Chem. Soc.*, London, 2, 51; Fresenius: *Ztschr. anal. Chem.*, 16, 339; Lunge : *J. prakt. Chem.*, 40, 239.

<sup>2</sup> Bull. U. S. Geol. Survey, 148, 1897.

this statement entirely and rather than dehydrate for silica we have precipitated the sulphuric acid directly in the acidulated aqueous solution of the fusion. We have never found any silica in the barium sulphate so obtained, but if its presence is feared it may be readily removed with a little hydrofluoric and sulphuric acids.

How considerable the contamination of the evaporating solution may be is plain from the experiment of E. von Meyer<sup>1</sup> who found, after evaporating 2 liters of distilled water down to 50 cc. during six hours on the water-bath, the equivalent of 0.0426 gram barium sulphate present.

A third objection and the most serious of all is against the separation of iron and alumina by boiling out the excess of ammonia. It is well known that iron can only be precipitated free from sulphur in a solution containing the latter by adding a distinct excess of ammonia to the moderately warm solution, heating a few minutes on the water-bath and filtering immediately. Only in this way can the formation of insoluble basic sulphates be prevented. Boiling the solution is, of all things, to be avoided. Lunge<sup>2</sup> states that correct results can only be obtained by adhering strictly to this procedure and that deviations lead to serious errors.

The check analyses made by the authors do not controvert the criticisms just made as the asphalt analyzed was said to be very pure and was presumably free from mineral matter.

Finally, in view of the recognized tendency of barium sulphate to drag down with it other mineral constituents of the solution and barium salts of other acids present, what must be said of precipitating sulphuric acid in the presence of ammonium oxalate and the alkaline chlorides from 30 grams of mixed carbonate and nitrate?

Our preference is given to Eschka's method following the details as described by Heath.<sup>3</sup> The Eschka method is admittedly the best for the determination of sulphur in bituminous coals. The problem here is a very similar one. In addition to its convenience and rapidity the Eschka method has the

<sup>1</sup> *J. prakt. Chem.*, 42, 267; see also Gunning : *Ztschr. anal. Chem.*, 7, 480; Alex : *Ibid.*, 10, 246; Wagner : *Ibid.*, 20, 323; Lieben : *Ibid.*, 32, 214; Privozink : *Ber. d. chem. Ges.*, 25, 2200.

<sup>2</sup> *Chem. News*, 71, 132; *J. prakt. Chem.*, 40, 239.

<sup>3</sup> This Journal, 20, 630.

advantage of leaving the iron, lime, and alumina insoluble at the start and only a small quantity of alkali is introduced into the analysis.

As for the mineral constituents they are better determined on a separate portion. Their accurate determination is made all the more difficult by the presence of an excessive amount of alkali metals as in Peckham's method.

Our practice has been to heat the asphalt at a low temperature in a platinum dish, slowly driving off the volatile constituents in such a way that the asphalt does not burn. At the end the temperature may be raised and the remaining organic matter burned without danger of loss.

The ash is extracted with hydrochloric acid and any insoluble residue fused with a small amount of the mixed carbonates. The solution of the fusion in hydrochloric acid is added to the other and the analysis proceeded with as usual. In this way the quantity of alkaline salts is reduced to a minimum.

Time is actually lost by determining the metals and sulphur in one portion as the determination of the latter must wait until the metals have been separated.

In all but two of the asphalt analyses of Dr. Day, as quoted by Messrs. Peckham, the decimal point is misplaced, making the per cent. sulphur far less than it should be.

LABORATORY OF RICKETTS AND BANKS, NEW YORK.

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## THE DETERMINATION OF NICKEL IN NICKEL ORES.

BY A. C. LANGMUIR.

Received November 24, 1899.

GEORGE WILLIAM SARGENT'S paper on the "Determination of Nickel in Nickel-Steel" in the October number of this Journal, prompts me to publish a somewhat similar method for the determination of nickel in its ores, which has been in use in this laboratory for several months with excellent results. It is particularly advantageous in all cases in which a relatively small quantity of nickel is to be separated from a large amount of iron and surpasses all other methods, such as the basic acetate, basic carbonate, or ammonia separations.

One gram of the ore is covered in a No. 2 Griffin's beaker



with 15 cc. concentrated nitric acid. One or two cc. of liquid bromine is added and the contents are gently heated until the bromine is expelled. The solution is then boiled down almost to dryness. Bromine in combination with nitric acid effects so thorough an oxidation that no sulphur bead can form. This reaction may also be applied in the analysis of copper mattes, where it is often necessary to filter off the sulphur bead which usually forms after the treatment with nitric acid and to roast it to recover the small amount of undecomposed sulphide which it invariably contains. The addition of bromine renders this extra operation entirely unnecessary.

After expelling the excess of nitric acid, about 50 cc. of concentrated hydrochloric acid are to be added and the solution slowly boiled down to 5 cc. The nitric acid is expelled and any residue carrying nickel and insoluble in nitric acid is brought into solution—at least in the ores handled by us.

Dilute to 250 cc. with hot water and pass hydrogen sulphide to remove copper, etc. Filter and boil the filtrate to expel hydrogen sulphide. Oxidize the ferrous iron by adding nitric acid to the boiling solution, drop by drop, carefully avoiding any excess. Cool slightly and add ammonia until distinctly alkaline. Filter and wash twice with hot water, catching the filtrate which will contain the bulk of the nickel in a large casserole and boil it down while the remaining operations are being performed.

Dissolve the ferric hydrate which carries a considerable amount of nickel in warm dilute hydrochloric acid. Wash into a casserole and boil down rapidly until pasty. Add about 10 cc. of hydrochloric acid (1.10 sp. gr.), warm slightly, rinse into a 250 cc. separating funnel with acid of the same strength, keeping the volume down to 50 cc., if possible, and cool thoroughly. Add now 40 cc. of C. P. ether and agitate vigorously at least five minutes. Invert the funnel occasionally and open the stop-cock cautiously to lower the pressure. The ferric chloride gradually dissolves in the ether leaving the nickel, aluminum, and any cobalt or manganese in the aqueous solution as chlorides.

The first solution obtained by boiling down the nitric acid residue with 50 cc. of hydrochloric acid cannot be profitably treated by the ether separation. On account of the sulphuric

acid formed by the oxidation of the sulphur, the removal of the iron by ether is far from complete. The sulphuric acid must be separated from the iron by an ammonia separation so that a solution containing only chlorides may be obtained. There is almost always some slight loss of solution in the treatment with ether in the separatory funnel, but any error from this source becomes negligible if the bulk of the nickel is first separated by ammonia.

After agitating, the funnel is allowed to stand a few minutes and the water solution is drawn off into a second funnel. The ether solution is washed twice with a few cc. of hydrochloric acid (sp. gr. 1.10), the washings being caught in the second funnel. Mr. Sargent contents himself with one ether treatment but we have always found it advisable to remove the iron still remaining with the nickel by a second agitation with 40 cc. of ether. The second operation is carried out in the same way as the first.

The aqueous solution and washings are run into a beaker, the dissolved ether is expelled by boiling, bromine water is added until the solution is strongly colored, and the iron, aluminum and any manganese present are separated by adding ammonia to alkalinity and boiling. If the ether treatment has been properly carried out, a mere trace of iron remains with the nickel and the precipitate may be caught on a 9 cm. paper. The precipitate obtained as above is dissolved in a little hydrochloric acid, bromine is added, and the precipitation with ammonia is repeated. The combined filtrates and washings are added to the casserole containing the now concentrated filtrate from the first ferric hydrate precipitate. The contents of the casserole which now contain all of the nickel in the ore are concentrated to 100 cc. or until ammonium chloride begins to separate. Fifty cc. of concentrated nitric acid are added and the solution is slowly boiled down almost to dryness. In this way the ammonium chloride is entirely destroyed. Ammonium nitrate is unchanged; hence the necessity for avoiding an excess in the oxidation of the ferrous iron. We are now able to concentrate the solution to a volume of a few cc. without the separation of any salts. Ten cc. of concentrated sulphuric acid are added and the casserole heated until dense fumes appear and the nitric acid is entirely

expelled. After cooling, dilute with 100 cc. cold water, boil, rinse into the high beaker used for electrolytic determinations, neutralize with ammonia, and add 25 cc. in excess. Dilute to 200 to 250 cc., insert the spiral and the weighed platinum cylinder, and electrolyze with a strong current,—we have used 1.2 amperes. The precipitation of the nickel is generally complete within three hours.

The separation of iron and nickel by ether has not as yet been used in the analysis of nickel ores, or mattes. It is unequalled for cleanliness, rapidity, and accuracy, and deserves the first place among the many methods proposed for the separation of iron and nickel.

The ammonia separation has proved particularly untrustworthy in our hands. Three and even four separations fail to remove the nickel, even if the acid solution containing the iron be poured into water containing an excess of ammonia.

The ready means afforded for destroying almost unlimited quantities of ammonium chloride by boiling down with an excess of nitric acid is not new, having been suggested long ago by Lawrence Smith in connection with his well-known method for alkali determinations. Yet it has been strangely neglected and we believe has never been used in the analysis of nickel ores, where it is particularly useful as it enables us to avoid the troublesome and inaccurate separation of the nickel as sulphide.

The solutions to be tested for nickel, ordinarily obtained in analysis, are choked with ammonium chloride, which prevents the concentration of the solution and necessitates the preliminary separation of the nickel from a dilute solution of sulphide. The difficulties in the way of precipitating and washing nickel sulphide without loss in the filtrate or washings are too well-known to need repetition.

In some analyses made by the author before his adoption of the ether method it was necessary to test for traces of nickel in several samples of steel. At least 5 grams had to be taken and the ammonium chloride accumulating in the filtrates from the ammonia separations of the iron was so large in amount that concentration to a bulk in which ammonium sulphide would reveal nickel was out of the question. But by boiling down slowly, with copious additions of nitric acid, it was possible to

destroy all the ammonium chloride and to finally test for nickel in a volume of some 15 cc. under ideal conditions.

The ether separation, as based on the solubility of ferric chloride in ether under the above conditions is, in all probability, not restricted to the determination of nickel or aluminum, but may possibly be applied in the separation of small amounts of zinc from iron. The separation of uranium and iron by ammonium carbonate and sulphide is far from satisfactory if the uranium be small in amount. Possibly in this case as well, the ether treatment may result in a decided improvement.

LABORATORY OF RICKETTS AND BANKS,  
NEW YORK.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 16.]

### LABORATORY METHOD FOR THE CONTINUOUS AND UNIFORM GENERATION OF ACETYLENE, AND FOR ITS PURIFICATION.

BY J. A. MATHEWS.

Received January 2, 1900.

FOR most purposes in which it is desired to employ a stream of acetylene, no purification is necessary, provided the gas has been properly generated from the usual quality of commercial carbide now being produced. Analyses from various sources show that the impurities in acetylene from this source rarely amount to 1 per cent. and a good part of this is likely to be nitrogen. The combined amounts of hydrogen sulphide, hydrogen phosphide, and ammonia seldom exceed 0.2 per cent. In order that the amount of impurities may be as small as possible it is necessary that the gas be produced in the cold. This cannot be done when water is allowed to drip slowly upon the carbide, and furthermore this method causes the gas to be given off spasmodically and the lime residue often bubbles or froths to such an extent that solid matter in considerable amounts may be carried over with the gas. In obviating all these difficulties the following method has proved successful.

The fragments of calcium carbide are placed in a wide-mouthed bottle. They may, with advantage, be suspended in a basket of coarse wire netting, which will keep the carbide away from the

lime residue, and also allow it to be withdrawn at any time. The carbide is covered with an abundance of absolute or 95 per cent. alcohol, and the bottle closed with a two-hole stopper. Through one hole water can be led from a reservoir bottle, and in the other an outflow tube is fitted. If 95 per cent. alcohol is used, the water therein serves to start the generation of acetylene and to expel the air from the apparatus. If, now, water be added drop by drop it comes slowly into contact with the carbide and a steady production of acetylene results. Unless the amount of alcohol present is very small and the rate of generation very rapid, no material rise in temperature ensues. After the addition of water has been stopped, the evolution of gas may be allowed to proceed until the bubbling ceases; the alcohol may then be decanted from the residue and distilled, and, rejecting the first few cubic centimeters, the rest of the distillate will be nearly absolute alcohol.

If it is desired to purify the acetylene, any one or more of several methods may be employed. No single purifying agent which has as yet been advocated, meets all the requirements. For general convenience and thoroughness the following combination of methods is suggested:

The acetylene generated as described above is passed into a solution of 15.6 parts of crystallized copper sulphate in 100 parts of water, to which is added 5 parts of dilute sulphuric acid,<sup>1</sup> 1 volume of sulphuric acid to 4 volumes of water. This solution, besides retaining any vapor of alcohol and also the ammonia and hydrogen sulphide, is especially useful for absorbing hydrogen phosphide. As an additional safeguard the acetylene is next passed through one or two towers filled with coarse bits of pumice stone which have been saturated with an acetic or sulphuric acid solution of chromic acid;<sup>2</sup> or, in place of a second tower, a strong sulphuric acid solution of chromic acid may be used. By this means any of the three chief impurities, which might escape absorption in the copper sulphate solution, will be completely oxidized. A small amount of these purifying materials will serve for a large volume of gas, and the acetylene should issue both dry and pure and possessing a faint and agreeable odor.

<sup>1</sup> Hempel and Kahl: *Ztschr. angew. Chem.*, 53, 1898.

<sup>2</sup> Ullmann: *J. für. Gasbeleucht.*, 42, 198, 374 (1899).

A return of the strong, irritating odor indicates that the purifiers have become exhausted.

The purification of acetylene by means of moist chloride of lime or sodium hypochlorite, as suggested by Odernheimer<sup>1</sup> and Lunge<sup>2</sup> or as modified by Wolff<sup>3</sup>, is impracticable because of the instability of the solutions and because chlorine and chlorination products of acetylene are produced, which must then be removed by lime. Frank's method,<sup>4</sup> using strongly acid solutions of copper or iron chloride, does not seem very efficient, nor is the employment of bromine as a purifier convenient for laboratory use. The combination of Hempel's and Ullmann's methods seems to meet all the requirements and is easily and conveniently arranged.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 17.]

## THE CARBIDE OF GOLD.

BY J. A. MATHEWS AND L. L. WATTERS.

Received January 2, 1900.

EXPLOSIVE compounds resulting from the action of acetylene or coal-gas upon alkaline solutions of cuprous, argentous and mercuric salts have been known for many years. These compounds are for the most part flocculent precipitates which retain water with more or less tenacity, and at temperatures which will render them anhydrous they are apt to explode violently. The earlier investigators of these acetylides did not recognize them as true carbides and their analyses show the presence of hydrogen and oxygen, which are reported as constituent atoms of the molecule. Berthelot,<sup>5</sup> who did a great deal of work upon acetylene derivatives, speaks of copper acetylide as "cupro-acetyloxide," and gives it the formula  $(C_2Cu_2H)_2O$ . Reboul<sup>6</sup> gives silver acetylide as  $(C_2HAg)_2 + Ag_2O$  and Blochmann<sup>7</sup> gives respectively,  $C_2H_2Cu_2O$  and  $C_2H_2Ag_2O$ . All of these might better

<sup>1</sup> *Chem. Ztg.*, 22, 21.

<sup>2</sup> *Ztschr. angew. Chem.*, 651 (1897).

<sup>3</sup> *Chem. Ztg.*, 22, 281; Wolff treats the gas first to remove ammonia and then with hypochlorite, thus eliminating the danger of forming nitrogen chloride, which he says is possible.

<sup>4</sup> *Ztschr. angew. Chem.*, 1050 (1898).

<sup>5</sup> *Ann. chim. phys.* [4], 9, 425.

<sup>6</sup> *Compt. rend.*, 54, 1229.

<sup>7</sup> *Ann. Chem.* (Liebig), 173, 176, 177.

be written  $C_2Cu$ , or  $C_2Ag$ , plus more or less water. Miasnikoff<sup>1</sup> gives silver acetylide as  $C_2H_2Ag_2$ . Keiser<sup>2</sup> showed, however, that when properly dried these two acetylides are simply  $C_2Ag$ , and  $C_2Cu$ , and later<sup>3</sup> produced mercuric acetylide,  $HgC_2$ , which is also hydrated at the time of its formation.

Berthelot<sup>4</sup> seems to be authority for the statement which appears in a number of old chemical works, but for which these do not give him credit, that by passing acetylene through aurous thiosulphate, a yellow explosive precipitate is formed. He gives no analyses of the product and does not give any suggestions as to its probable constitution.

We have recently investigated this interesting compound, which proves to be analogous to the copper and silver compounds, its formula being aurous carbide,  $Au_2C_2$ .

In the preparation of aurous sodium thiosulphate we followed the method of Fordos and Gélis.<sup>5</sup> Pure auric chloride was dissolved in 50 parts of water; 3.2 parts of sodium thiosulphate were dissolved in the same amount of water. The solution of gold was added to the thiosulphate very slowly and with constant stirring. A slight odor of sulphur dioxide was noticed and a little sulphur separated.

The solution was filtered and the sodium aurous thiosulphate was precipitated with absolute alcohol. It was not recrystallized. The principal reaction is said to be



This compound forms a colorless precipitate, very soluble in water but insoluble in alcohol. To form aurous carbide an aqueous solution of the sodium aurous thiosulphate is made strongly alkaline with ammonia and a slow stream of acetylene passed through. The solution remains colorless for a short time and then becomes yellow and finally a yellow flocculent precipitate appears. In this respect it differs from silver and copper carbides, which form almost instantly and hence are used to test for the presence of minute quantities of acetylene. The precipitate is filtered off, washed with water and alcohol and dried in a desiccator over sulphuric acid.

<sup>1</sup> *Ann. Chem.* (Liebig), 118, 330.

<sup>2</sup> *Am. Chem. J.*, 14, 285.

<sup>3</sup> *Ibid.*, 15, 535.

<sup>4</sup> *Ann. chim. phys.* [4], 9, 425.

<sup>5</sup> *Ibid.*, [3], 13, 394, 1845.

*Properties.*—When thoroughly dried, the carbide of gold is highly explosive either upon rapid heating, by a blow or even by brushing with a camel's hair brush. The explosion generates sufficient heat to produce flame and the gold is left in an extremely finely divided condition and black. Carbide of gold is easily decomposed by hydrochloric acid giving acetylene and leaving a black residue of aurous chloride. The presence of acetylene was shown by passing it into ammoniacal silver nitrate, in which it produced silver acetylide. The aurous chloride was tested by boiling, which gave auric chloride and metallic gold. By boiling gold carbide with water it is decomposed into its constituents, no acetylene being produced. Cupric sulphate and neutral ferric chloride do not decompose it in the cold; when anhydrous it becomes darker in color and of a brown tint and if heated very gradually decomposes without explosion. This fact was made use of in the determination of gold. The sample to be analyzed was heated in the air-bath very slowly until a temperature of  $180^{\circ}$  to  $200^{\circ}$  was indicated, and then ignited in the flame of a Bunsen burner. The black mass becomes yellow by the burning off of the carbon and annealing of the gold. The analyses resulted as follows:

	Weight of sample.	Gold found.	Gold. Per cent.	Theory for $\text{Au}_2\text{C}_3$ .
I	0.029	0.0273	94.14	94.25
II	0.0174	0.0164	94.25	94.25

One sample of aurous carbide after two days in the desiccator lost no weight at  $100^{\circ}\text{C}$ . nor was loss experienced on renewed heating up to  $120^{\circ}\text{C}$ . Another sample that had not stood so long over sulphuric acid lost 0.0004 gram at  $100^{\circ}$ . By rapid heating in the air-bath explosions were obtained at various temperatures from  $83^{\circ}$  to  $157^{\circ}\text{C}$ . No attempt was made to secure especially uniform heat at all parts of the air-bath, but the thermometer bulb was in all cases very close to the dish containing the explosive compound. It seems then that the rate of heating has most to do with effecting the decomposition of gold acetylide. The violence of the explosion was shown by several unexpected explosions. In one case about 15 or 20 milligrams of the substance were on a watch-glass. In trying to remove a small fragment with the point of a knife, the whole



mass exploded with a sharp report and the watch-glass was broken into a score of pieces. In another instance while brushing some of the carbide from a filter-paper with a camel's hair brush into a dish, the particles adhering to the paper exploded with a loud report and flame and the filter-paper was badly torn but the bulk of the material, which was not over an inch or two away, was not exploded by the concussion. The same fact was noted in the first explosion above in which case the watch-glass was standing beside a crucible containing quite a large amount of dry gold carbide.

No other aurous solutions were tested with a view to obtaining gold carbide. From auric chloride in aqueous solution metallic gold is precipitated by acetylene.

A solution of auric chloride made alkaline with potassium hydroxide does not give a precipitate under similar conditions, nor does an aqueous or ammoniacal solution of potassium auric cyanide give a precipitate when acetylene is passed into it.

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### THE NATURE OF THE CHANGE FROM VIOLET TO GREEN IN SOLUTIONS OF CHROMIUM SALTS.

BY F. P. VENABLE.

Received January 22, 1900.

IN a recent number of this Journal<sup>1</sup> Whitney has reported further work upon this problem and at the same time criticized an article by Venable and Miller which had previously appeared upon the same subject.<sup>2</sup> As Mr Miller is no longer at work with me and I was, in the main, responsible, for the presentation and discussion with which Dr. Whitney finds fault, my name appears alone in this reply.

Whatever disinclination I may have felt to accept as final the previous efforts at determining the presence of free sulphuric acid in the green solutions, I can have none as to this recent admirable and conclusive direct determination of the acid by Whitney. It is, of course, of little importance to explain why an opinion was formed, unless truth is advanced by such explanation. I shall therefore only refer to two or three of the facts stated by Whitney as sufficient to convince one that free sul-

<sup>1</sup> This Journal, 21, 1075-1084.

<sup>2</sup> *Ibid.*, 20, 484-496.

phuric acid is present. I do this because I cannot verify them as facts.

1. Dr. Whitney states that the green solutions are acid to the usual indicators. We could draw no conclusions as to the difference between the solutions from this because both violet and green solutions are thus acid. This statement was made by us in the original article and has been carefully verified by me since reading Whitney's article. It is also supported by the experiments of Baubigny and Pechard. Furthermore, the mere fact that barium chloride is prevented from precipitating all of the sulphuric acid in the green solution cannot be taken as proving the presence of free sulphuric acid.

2. Whitney cites Recoura as stating that the "distillation of the green solution results in an acid distillate, while the violet salt may be heated above  $100^{\circ}\text{C}$ . without loss of acid." My experiments failed to verify this. I took 15 grams of the alum and dissolved it in 200 cc. of distilled water. This was then carefully distilled from an ordinary distilling flask connected with a condenser and the distillate treated in successive portions of 50 and 25 cc. until only about 25 cc. were left, without finding any acid. Beyond this point the temperature began to rise, portions splashed upon the sides became overheated, and acid distilled over. This was repeated with chromium sulphate with the same result. It was also repeated with ordinary potash alum with the same result. As the solution became very concentrated the temperature rose, portions were splashed upon the hot sides and acid distilled over. Lastly, it was repeated with 5 cc. of sulphuric acid in 200 cc. of water and no acid distilled over until most of the water had been driven off and the temperature had risen above  $100^{\circ}\text{C}$ . Manifestly this experiment of Recoura's can throw no light upon the presence or absence of free acid.

3. Krüger's statement that alcohol poured in a layer over the green solution takes up acid (something that gives an acid reaction) from the solution is only part of the truth for alcohol will do precisely the same thing when poured over the violet solution. In the course of a few hours the reaction is quite perceptible from both solutions. There is no change apparent in the color of the violet solution after four or five days' standing under the layer of alcohol.

After weighing the evidence then at hand I reached the conclusion that a satisfactory explanation of the change could scarcely be deduced from these and the other experiments.

And they did not seem to me to justify the construction of an equation and an elaborate formula for a hypothetical substance which was assumed to cause the green coloration, even if the presence of the free acid should be granted.

The exception is well taken by Whitney to our experiment with the decinormal solution of ammonia and explains a result which greatly puzzled us in the interpretation of our later work. We scarcely knew what value to attach to the experiment and so merely stated that "these experiments therefore agree with those of Baubigny and Pechard, but are at variance with the conclusions of the other authors mentioned." The agreement was, of course, only to the extent that "both solutions are acid" and that was all that was claimed for the experiment.

It seemed to us necessary to get under hand for analysis the body which gave the green coloration before any formula could be established for it. We therefore abandoned what we styled "indirect methods giving results capable of other explanations." We thought it more material to secure this body than to settle the question as to whether free acid or an acid sulphate was formed. Certainly any other line of research would always leave the body in question hypothetical. Hence in the latter part of the paper<sup>1</sup> the sentence occurs, "as the alcohol left is decidedly acid it must contain either free acid or an acid sulphate" and there was no further effort at settling this point.

The method which most commended itself to us for securing this compound was precipitation by means of alcohol. In this precipitate, in the case of the alum, we obtained the potassium sulphate along with the chromium compound and this blinded us to the true formula. A recalculation of the results of Mr. Miller's analyses, eliminating the potassium sulphate, and taking the mean of the experiments, gives as the ratio of the chromium to  $\text{SO}_4$ , 18.23 : 41.62. Now the ratio, calculated for the formula  $\text{Cr}_2\text{O}(\text{SO}_4)_2\cdot\text{SO}_4$ , is 18.23 : 41.99. Having then the direct determination of the free sulphuric acid from Whitney's last experiments and the gravimetric determination of the chromium

<sup>1</sup> This Journal, 20, 495.

and  $\text{SO}_4$  in the basic chromium sulphate from Miller's analysis, there can no longer be any reason for not accepting the equation given for the change :



The conclusion drawn in the article by Miller and myself was conservative and still stands ; namely, that the color of the green solutions was due to the formation of basic salts of chromium, green and uncrystallizable, thus confirming the explanation first suggested by Berzelius. To this must now be added that this formation is accompanied by the liberation of a portion of the combined acid, in the case of the alum corresponding to one-half of the total.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 18].

## ON THE DECOMPOSITION OF NICKEL CARBONYL IN SOLUTION.

BY VICTOR LENHER AND HERMANN A. LOOS.

Received January 12, 1900.

IT has been shown by Berthelot that nickel carbonyl in contact with moisture suffers decompositions of a more or less complex character. When nickel carbonyl is mixed with water according to Berthelot<sup>1</sup> there is formed a green compound which consists of hydrate of the oxide free from carbon. A portion of the nickel carbonyl at the same time escapes and is oxidized in moist air to a whitish compound. This same white compound Berthelot prepared in larger quantity by the slow oxidation with air and found it to contain 5.3 per cent. carbon, 53.3 per cent. nickel oxide ( $\text{NiO}$ ), and 40.1 per cent. water.

Mond<sup>2</sup> considers the green body formed when nickel carbonyl is exposed to damp air to be a carbonate of nickel of varying composition.

The deportment of nickel carbonyl in solution is different from that in the pure condition or as a gas, as is seen, for example, from the fact, that it will decompose in solution at  $60^\circ$ , whereas in the gaseous condition, it will not decompose until about  $150^\circ$ .

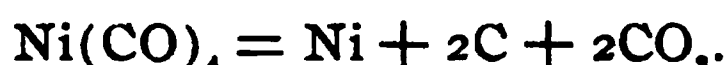
<sup>1</sup> *Compt. rend.*, 112, 1343; 113, 679.

<sup>2</sup> *Chem. News*, 64, 108; also *J. Soc. Chem. Ind.*, 11, 750.

In gaseous condition, heat decomposes it simply, into nickel and carbon monoxide.



In solution the action takes a different form and may be represented as follows :



It would not be surprising then to find that the solution would act differently than the pure substance, under the action of moisture or oxidation.

While working with nickel carbonyl dissolved in various organic solvents, such as chloroform, benzene, toluene, etc., it was found that the solutions on standing suffer decomposition with the formation of a green precipitate; this was probably due to the presence of more or less moisture, either in the solvent or in the surrounding atmosphere. That the precipitate is produced by the action of moisture is evidenced by the fact that the decomposition is more rapid when the solution is exposed to the air and still more rapid when moist air is bubbled through the solution.

A solution of nickel carbonyl will, after standing, suffer decomposition with the formation of a green to a brown gelatinous precipitate. In appearance, this precipitate is similar to that obtained by the action of water or moisture on pure liquid nickel carbonyl.

The precipitate formed from various solvents has been studied with a view of determining if possible its composition. The substance is evidently of very complex nature and is undoubtedly an oxidation product. When a solution of nickel carbonyl in acetone or chloroform is allowed to stand, a green gelatinous precipitate forms in a few hours. After a greater length of time the precipitation becomes complete, and on filtration, no nickel can be found in solution. This same decomposition takes place but more slowly in benzene, toluene, and methyl alcohol. The precipitate is colored light green to dark brown according to the solvent used, and according to the small amount of iron carbonyl which frequently contaminates the nickel carbonyl. The deportment of the solution in ethyl alcohol is peculiar. If this solution is mixed with an equal volume of water, a clear solution is

first obtained, but in a few minutes, it gelatinizes to a green translucent mass. This substance settles very slowly. On filtering off the precipitates and carefully drying, all assume a greenish color. Examination of this precipitate indicates that it is a decomposition product which contains nickel carbonyl and nickel hydroxide.

Analyses of the substance obtained from toluene gave the following results :

	Calculated for $\text{Ni(CO)}_4 \cdot 2\text{Ni(OH)}_2 \cdot 4\text{H}_2\text{O}$ .	I.	Found. II.
Carbon .....	11.19	11.66	11.38
Hydrogen .....	2.80	2.95	2.97
Nickel .....	41.26	42.82	42.68

As different samples gave results which differed slightly, it appears that the composition of the substance varies slightly as is apt to be the case in an oxidation product. A precipitate from benzene was found to contain 42.09 per cent. of nickel, while one from chloroform contained 42.81 per cent.

The precipitate carbonizes with sulphuric acid while with dilute acids carbon dioxide is evolved. Sodium or potassium hydroxide attacks the precipitate and apparently removes a portion, since after treatment with one of these alkalies and thoroughly washing, acids will no longer produce effervescence. Potassium iodide is without action; potassium cyanide dissolves it to a brown solution. It is insoluble in chloroform, benzene, toluene, petroleum ether, alcohol, acetone, methyl alcohol, or ether. Ammonium sulphide converts it to the black sulphide of nickel. Although the formula calculated for comparison with the analyses does not account for the evolution of carbon dioxide with an acid, yet this can be explained by the fact that carbon dioxide is invariably a result of the decomposition of nickel carbonyl in solution.

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#### ERRATUM.

In the December issue (1899), on page 1145, in the fourth line of table, for "calcium chloride" read "chloride of lime (bleaching powder)."

# THE JOURNAL

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### SUBSTITUTES FOR HYDROCHLORIC ACID IN TESTING CARBONATES.

BY JOSEPH W. RICHARDS AND NORMAN S. POWELL.

Received January 23, 1900.

THE following experiments were undertaken in the hope of finding a satisfactory substitute for hydrochloric acid in producing effervescence with natural carbonates. It is well-known that hydrochloric acid is difficult to carry in a portable set of apparatus, and while it is entirely satisfactory to use it in the laboratory, yet it would be very desirable to have some solid material to replace it in a portable testing outfit.

The materials tested as substitutes were potassium acid sulphate, citric acid, tartaric acid, and oxalic acid. These were made into solutions of the strength of 4 parts of water to 1 part of salt or acid, or 20 per cent. solutions. This would correspond roughly to dissolving a piece the size of a pea in 1 cc. of water. Such a solution, in a test-tube, makes a suitable reagent. Oxalic acid, however, requires about twice as much water as above given for complete solution. Therefore this was of about 10 per cent. strength.

The carbonates tested were as follows: calcite, dolomite, magnesite, siderite, rhodochrosite, smithsonite, aragonite, with-

ite, strontianite, cerussite, barytocalcite, phosgenite, malachite, azurite, hydrozincite, lansfordite.

These were taken as representative of the common natural carbonates. Each mineral both as lump and powder was tested in cold, warm, and nearly boiling solutions of each reagent. For convenience in recording the results, the following numbers are used in the table to designate the degrees of effervescence.

0. No action.
1. Gas evolved in traces.
2. Gas evolved faintly, but plainly.
3. Gas evolved freely, not strongly.
4. Gas evolved strongly.
5. Gas evolved violently.

The results were, in general, that the powder was acted on more violently than the lump, and the action was stronger as the solution was warmer; but there were exceptions to these rules, which will be noted.

#### POTASSIUM ACID SULPHATE.

(20 per cent. solution.)

*Cold*: Nearly half the carbonates were unacted on, or acted on only in traces. *Warm*: All were acted upon, but cerussite, strontianite and phosgenite only faintly, and witherite in traces. In these four cases, the insolubility of the sulphates of the bases present explains the faint action. *Hot*: All were acted upon, the majority strongly, but cerussite and phosgenite yet faintly, and witherite only in traces, as before. With careful observation, this test should positively detect any carbonate with the possible exception of witherite.

The action of this reagent on *calcite*, *dolomite*, and *magnesite*, is interesting. In lukewarm solutions the powders effervesce as follows: calcite strongly, dolomite freely but not strongly, and magnesite only faintly. This corresponds to their order with hydrochloric acid. But when a *lump* of each is put into *hot* solution, nearly boiling, the order is reversed: Calcite effervesces freely, dolomite strongly, and magnesite violently. The differences are very easily noted, and make this test quite practicable for distinguishing between these minerals. For distinguishing calcite from dolomite, the action of the cold solution on the



powder is also decisive: calcite powder effervesces strongly, at once; dolomite powder only faintly.

## OXALIC ACID.

(10 per cent. solution.)

*Cold*: About half the carbonates were unacted upon. *Warm*: All were acted upon, but nearly half only faintly; only two strongly. *Hot*: All were acted upon, the majority freely, a few only faintly, only one violently. With ordinary care in observing, this test is satisfactory for all the carbonates tried.

With calcite, dolomite, and magnesite, the effervescence increased in the order given. In cold solution, calcite was unacted upon either in lump or powder; dolomite showed traces of gas; magnesite showed gas evolved plainly. In hot solution, calcite effervesced freely but not strongly, dolomite strongly, magnesite violently. The insolubility of calcium oxalate accounts, of course, for this behavior.

## CITRIC ACID.

(20 per cent. solution.)

*Cold*: About half the carbonates were unacted on, or acted on only in traces. *Warm*: All were acted on, about one-third faintly, one-third freely, and one-third strongly. *Hot*: All were acted upon, only three (phosgenite, rhodochrosite, and azurite), as low as freely, the rest being strongly to violently affected.

We recommend this reagent as entirely satisfactory, for testing either lump or powder in hot solution. This reagent also distinguishes clearly calcite from dolomite, for in cold solution calcite effervesces faintly to freely, and dolomite is entirely unacted upon.

## TARTARIC ACID.

(20 per cent. solution.)

*Cold*: Only three carbonates were unacted upon, smithsonite, rhodochrosite, and phosgenite; about half were acted on faintly, the rest freely, one strongly. *Warm*: All were acted upon, one-third faintly, one-third freely, one-third strongly. *Hot*: All acted upon, only rhodochrosite and phosgenite as low as *freely*

		POTASSIUM HYDROSULPHATE. 20 % solution.			CITRIC ACID. 20 % solution.			TARTARIC ACID. 20 % solution.			OXALIC ACID. 10 % sol. with excess of undissolved acid.		
		Cold	Warm	Hot	Cold	Warm	Hot	Cold	Warm	Hot	Cold	Warm	Hot
Calcite .....	{ Lump Powder	1 then stops 4 at once	2	3	1-2	3½	4	2-3	3½	4½	0	1	3
Dolomite .....	{ Lump Powder	1 then stops	2	4	2-3	4	5	3-3½	4	4½	0	2	3½
Magnesite .....	{ Lump Powder	2	3	4	0	2	4	1½-1	2	4	1	2	3
	{ Lump Powder	2	3	4	0	3	4	1	2	4½	1	3	4
	{ Lump Powder	2	3	5	2-1	2	4	2-1	2	4	2-1	3	4
	{ Lump Powder	2	2	5	0	2	4	1	2	4½	1-2	3	5
Cerussite .....	{ Lump Powder	2-1-0	2	3	1	2	4	1-2	3	4½	1	2	3½
	{ Lump Powder	1	1	2	3-0	3	4	2-2½	2½	4	1	3	3½
Smithsonite.....	{ Lump Powder	0	2	3½	0	2	4-3½	0	2	4	0	2	4
	{ Lump Powder	1	3	4½	0	2	4	0	2	4½	0	3	4½
Witherite.....	{ Lump Powder	0	1	1	2	3	4	2½	3	4½	4-1	2	4
	{ Lump Powder	1	1	1	3	4	5	3	4	5	4-1	2	4
Strontianite ...	{ Lump Powder	3-1	1	3-1	1	3	4	2	3	4	1	3	4
	{ Lump Powder	3	2	3	2	3½	4	3	4	5	3	4	4½
Barytocalcite ..	{ Lump Powder	2½-2	3	3½	2	3	4	2½	4	5	3-1	2½	4
	{ Lump Powder	3	3½	4	3	4	5	3	4½	5+	3-1	3	4
Siderite .....	{ Lump Powder	1	2	3-2	1	3	4-3½	2	2½	3½-3	0	2½	3½-3
	{ Lump Powder	1	2½	3	1½	3	4	1	3	4	0	3	4½
Malachite .....	{ Lump Powder	3	4	4½	2	3	4	2½	3	4	2½	3	4
	{ Lump Powder	3½	4½	5	3	4	5	3	4	5	3	4	4½
Azurite .....	{ Lump Powder	2½	3½	4½	0	2	3½	0	2	3½-3	1	2	3-2
	{ Lump Powder	3½	4½	5	0	3	4	2	3	4	3-2	3	3
Hydrozincite...	{ Lump Powder	3	4	5	3	3½	4½	2	2	3½-3	1½	2	3-2
	{ Lump Powder	3½	4	5	3½	4½	5	3	3	4	1	2	2½
Arazoneite.....	{ Lump Powder	2½-2	2	3½-3	3	3	4½-4	2	3½	4½	2-1-0	2	4-3
	{ Lump Powder	3	3½	4	3	4	5	3	4	5	3	3½	4½
Phosgenite ....	{ Lump Powder	1	1	2	0	2	3	0	2	3-2	1	2	3-2
	{ Lump Powder	2	2	2½	0	3	4-3	1	3	3½	2	2½	3-2
Lansfordite ....	{ Lump Powder	3	4	5	3½	4	5	3½	4	5	3½	4	5
	{ Lump Powder	4	4½	5	4	4½	5	4	4½	5	4	4½	5
Rhodochrosite .	{ Lump Powder	1	2½	3-2	1	2½	3	0	2½	3½-2	1	2	3-2
	{ Lump Powder	0	2	3½	0	2	3½-3	0	2½	3½-3	0	2	3½-3

5. Violently. 4 Strongly. 3. Freely, not strong. 2. Faintly, but plainly. 1. In traces. 0. No action.

*not strongly*, the rest being about half *strongly* and half *violently* affected. This reagent is satisfactory even in warm solution, and still better in hot solution.

Unlike citric acid, it causes dolomite to effervesce in traces even in the cold, while calcite is made to effervesce freely. The distinction is therefore not quite so sharp as with citric acid.

#### CONCLUSION.

Tartaric acid is the best of the four reagents; citric acid is a close second. Both give satisfactory results in every case tested, using lump or powder in hot solution. Oxalic acid also gives effervescence in every case, in hot solution, and is indeed a practicable reagent, but not so strong as the preceding. Potassium acid sulphate is satisfactory except in the cases of witherite and phosgenite; the rest average low, but the effervescence is sufficient to be easily observed. Bearing these exceptions in mind, it can be used if the other reagents are not at hand.

Some sulphides also effervesce with each of the reagents, giving off hydrogen sulphide, as with hydrochloric acid, and the odor of the gas coming off should therefore be tested, to make sure that the material is not a sulphide.

LEHIGH UNIVERSITY,  
January 18, 1900.

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## REGULATIONS FOR THE TESTING OF THERMOMETERS.<sup>1</sup>

[As Adopted by the Physikalisch-Technische Reichsanstalt, April 1, 1898.]

### I. PRELIMINARY REMARKS.

1. Glass thermometers filled with mercury, alcohol, toluene, or any other suitable liquid will be accepted for testing. They will be distinguished as:

*a.* Standard normal thermometers [*Haupt-Normalthermometer*];

*b.* Thermometers for scientific purposes (laboratory thermometers);

*c.* Thermometers for meteorological purposes and for estimating altitudes by boiling-point determinations;

*d.* Thermometers for technical purposes (factory thermometers);

<sup>1</sup> Translated for the use of the Committee on Standards and for the Journal of the Society by C. E. Linebarger.

- e.* Thermometers for medical purposes (clinical thermometers);
- f.* Thermometers for household or domestic use (window-, room-, bath-thermometers, etc.).

The *standard normal thermometers* will be tested only at the Physikalisch-Technische Reichsanstalt, the thermometers for household use only at the testing bureau in Ilmenau.

The Physikalisch-Technische Reichsanstalt is to decide as to the acceptance of thermometers other than the above, unless this is provided for in what follows, although questions as to acceptance may be addressed to the testing bureau at Ilmenau.

Such faults in the construction of all thermometers sent in to be tested, as may give rise to inaccuracies or irregularities in their temperature indications or render their reading too difficult are to be avoided.

2. The testing is done in two stages—the preliminary testing [*Vorprüfung*] and the main testing [*Hauptprüfung*]. The former takes into account all the regulations given in paragraphs 4 to 10, while the latter consists of a regular thermometric examination, beginning with observations, lasting for at least eight days, on the constancy of the indications of the thermometer (by means of determinations of the freezing-point and the like).

The type of the instrument determines whether the further tests shall involve :

- a.* A determination of the fundamental interval<sup>1</sup> by calibration and comparison with normal thermometers,
- b.* or only a comparison with normal thermometers in thermostats.

Whenever the divisions on the instrument permit, the amount of the depression of the freezing-point will always be determined and stated in the certificate.

In the testing of a maximum or minimum thermometer (for medical, meteorological, or other purposes), besides the comparison stated in *b*, experiments will be made to ascertain whether the instrument works properly. The errors in both series of tests for such thermometers should not differ when the divisions are

<sup>1</sup> [The fundamental interval is the scale interval between the normal boiling-point and the normal freezing-point, the latter being taken at the lowest position observed.]

$\frac{1}{16}^{\circ}$  or  $\frac{1}{8}^{\circ}$  by more than  $0.08^{\circ}$  C.  
 $\frac{1}{8}^{\circ}$  "  $\frac{1}{8}^{\circ}$  " " "  $0.2^{\circ}$  C.

The differences in the readings of maximum thermometers *at* a given temperature and *after* cooling, should not in the case of clinical thermometers amount to more than  $0.15^{\circ}$  C. In the case of maximum thermometers of other kinds the allowable differences are to be estimated from the length of the mercury column.

Tests will also be made to ascertain whether the device for recording the maximum temperature offers too great a resistance when the mercury is shaken down.

3. The fundamental temperature scale shall be that of the hydrogen thermometer as adopted for the international system of weights and measures according to a resolution of the *Bureau international des Poids et Mesures*, on October 15, 1887.

## II. GENERAL REGULATIONS.

4. The glass used in the construction of the thermometers should have the least possible thermal hysteresis [*thermische Nachwirkung*]. When glass is employed whose hysteresis is not sufficiently known or which is found to be too great, the thermometers must be allowed to stand from one to four months, the sender being notified of such action.

Thermometers which are to be tested at temperatures above  $100^{\circ}$  C., as well as all finer thermometers such as listed in paragraph 1, under *a*, *b*, and *c*, must be subjected to an artificial aging process before they are sent in. This consists in heating them for ten to thirty hours, according to the temperatures they are intended to indicate, to the highest temperature they register, and then cooling them slowly. Notice must therefore be given when the thermometers are sent in as to whether this heating has been done or not.

Thermometers reading to  $550^{\circ}$  C. should be made of Jena borosilicate glass 59<sup>III</sup> or some similar difficultly fusible glass; those reading to  $420^{\circ}$  may also be made of Jena normal thermometer glass 16<sup>III</sup> (with red-violet stripe) or of Greiner and Friedrichs' resistance glass (with blue stripe).

5. The capillary tube must be clean and of uniform bore. Thermometers of the types *a*, *b*, *c*, and *d*, in paragraph 1, are to have a pear-shaped bulb blown in their upper end. Bulbs blown

in the capillary tube itself must be there for a purpose and must not occasion a narrowing of the adjacent parts of the tube (unless, indeed, such constrictions are meant to serve a special object), which might cause a separation of the mercury during transportation or use. The upper end of the capillary must be in plain sight and not covered by the cap.

6. The mercury must be pure and dry and threads of it must not break off when it is retreating into the bulb. The mercury column should not separate at any place when the thermometer is inverted without jarring. Exceptions to this may be allowed in the case of thermometers with very long stems or large bores or with especially large bulbs.

Any other liquids used to fill the thermometers must be of such a nature that, when the column of liquid is retreating into the bulb, visible drops do not remain behind, and the coloring-matter that may be employed does not separate out.

The use of liquids with too low boiling-points is to be avoided as there is danger of their distilling over into the end of the capillary.

Thermometers designed to measure temperatures over  $280^{\circ}\text{C}$ . must be filled above the mercury with some dry gas (nitrogen, carbon dioxide, and the like) under proper pressure.

7. The scale-divisions must be durable and without any easily apparent errors. In the case of enclosed thermometers<sup>1</sup> [*Einschluss-thermometer*] the scale-divisions must be as close as possible to the capillary so as to insure definite and accurate readings at all positions.

The length of the shortest scale-division on a stem thermometer<sup>2</sup> [*Stab-thermometer*] should in general be at least  $\frac{1}{8}$  of the circumference of the tube.

The nature of the division must be designated by the words *hunderttheilig* [“hundred-degreed”], Celsius, etc., and the divisions must be plainly numbered. Division marks must not be placed on widened parts of the capillary.

Division marks should not extend *unnecessarily far* above the temperature interval to be employed. Still a few divisions must

<sup>1</sup> Enclosed thermometers are such as have a small capillary tube lying against a scale and all enclosed in a larger tube.

<sup>2</sup> In stem thermometers the scale-divisions are cut or etched directly on the capillary tube.

always be marked above the highest and below the lowest of the parts of the scale to be tested.

Thermometers with Réaumur scales will not be tested. Exception to this rule will be made until the end of 1900 in the case of thermometers for technical use (*cf.* paragraph 1, *d*).

8. The scales of enclosed thermometers must be fastened securely and firmly, but must permit of free expansion without bending in one direction with reference to the enclosing tube. Thermometers with paper scales will be tested only up to 60° C.

The position of the scales with reference to the capillary or the enclosing tube is to be controlled by means of a mark which, when possible, will be placed on the *right-hand* side of the thermometer and is in no wise to interfere with the reading at that point.

The enclosing tube of enclosed thermometers should, unless exceptions be allowed according to the special regulations (paragraphs 11 to 16), be fused together at the upper end or be provided with a second mark in the vicinity of the end of the scale.

9. Only thermometers of the types *d* and *f* (technical and household thermometers) may have detachable scales. The tubes of such thermometers must be firmly fastened, must lie close to the scale, and must bear marks to control their position. The fastenings must be so arranged that they may be removed for testing and marking.

Thermometers with detachable scales will have both tube and scale marked (*cf.* paragraph 17).

10. Thermometers may bear the maker's number, trade-mark, etc., but nonsensical marks and such as are contrary to the results of the testing will not be permitted.

Maximum and minimum thermometers must be specially marked as such.

There must be on every thermometer sufficient room to place the official mark or stencil (*cf.* paragraph 17), and any other needed marks (*cf.* paragraph 18).

### III. SPECIAL REGULATIONS.

In what follows are given the requirements for testing and the allowable limits of error for the different types of thermometers listed in paragraph 1.

11. *Standard normal thermometers* must be mercury-in-glass thermometers, bearing the points 0 and 100 on their scale and must permit of direct calibration. They will be tested exclusively by the Physikalisch-Technische Reichsanstalt.

The divisions of these thermometers must be uniform and made without regard to the errors of calibration. The errors of division should not exceed  $\frac{1}{10}$ , and the width of a mark  $\frac{1}{10}$ , of the smallest interval.

The capillary tube must have a pear-shaped widening at its upper end and must be free from air. The examination of these thermometers will be made between the temperature-limits,  $-30^{\circ}$  to  $+100^{\circ}$  C. and for every  $10^{\circ}$  at least.

The limits of error are :

1. For the fundamental interval,  $0.10^{\circ}$  C.;
2. For the error of calibration as the difference of the greatest deviations,  $0.25^{\circ}$  C.;
3. The depression of the freezing-point after a half-hour's heating to  $100^{\circ}$  C. and subsequent imbedding of the thermometer in ice for five minutes should not amount to more than  $0.10^{\circ}$  C.

The certificate will give in  $0.001^{\circ}$  the corrections for calibration, fundamental interval, freezing-point, and reduction to the gas-thermometer and also the aggregate error rounded off to  $0.01^{\circ}$ .

12. *Laboratory thermometers* are such as are employed in scientific and technical investigations in the laboratory for the measurement of temperatures from  $-80^{\circ}$  to  $+550^{\circ}$  C.<sup>1</sup>

The limits of error are :

For the temperature interval	When the scale is divided into integral degrees or multiples thereof.	fractions of a degree.
from $-80^{\circ}$ to $-30^{\circ}$	$2^{\circ}$ C.	$1^{\circ}$ C.
" $-30^{\circ}$ " $0^{\circ}$	1	0.5
" $0^{\circ}$ " $100^{\circ}$	0.5	0.25
" $100^{\circ}$ " $200^{\circ}$	1	0.5
" $200^{\circ}$ " $300^{\circ}$	2	1
" $300^{\circ}$ " $400^{\circ}$	3	2
" $400^{\circ}$ " $550^{\circ}$	5	4

<sup>1</sup> Until further notice the scale of the air thermometer shall be standard for temperatures over  $100^{\circ}$  C., as the international agreement (cf. paragraph 3) has reference only to the interval between  $0^{\circ}$  and  $100^{\circ}$ , the comparison with the hydrogen thermometer having not yet been finished.



Tests are made when the divisions are in  
 $\frac{1}{10}^{\circ}$  C. for at least every  $10^{\circ}$ ,  
 $\frac{1}{3}^{\circ}$  C. for at least every  $15^{\circ}$ ,  
 $\frac{1}{2}$  or  $\frac{1}{4}^{\circ}$  C. for at least every  $20^{\circ}$ , when the length of  $10^{\circ}$  is more than 40 mm.

$\frac{1}{2}$  or  $\frac{1}{4}^{\circ}$  C. for at least every  $25^{\circ}$ , when the length of  $10^{\circ}$  is more than 20 mm. and less than 40 mm.

$\frac{1}{2}$  or  $\frac{1}{4}^{\circ}$  C. for at least every  $50^{\circ}$ , when the length of  $10^{\circ}$  is more than 8 mm. and less than 20 mm.

$\frac{1}{2}$  or  $\frac{1}{4}^{\circ}$  C. for at least every  $100^{\circ}$ , when the length of  $10^{\circ}$  is less than 8 mm.

13. (1) By *meteorological thermometers* are meant those used in finding the temperature of the air, of natural waters, of the earth's crust, of the sun's radiation, of the dew-point, etc. The scale may embrace any interval between  $-70^{\circ}$  and  $+100^{\circ}$  C.

Tests are made

When the divisions are in		Limits of error.
$\frac{1}{3}$ or $\frac{1}{10}^{\circ}$ C.	For every $10^{\circ}$ , at least.	Same as given in
$\frac{1}{2}$ " $\frac{1}{4}^{\circ}$ "	" " $20^{\circ}$ , " "	paragraph 12.

(2) Thermometers for the measurement of altitudes by boiling-point determinations may be divided either in centigrade degrees or in millimeters of tension of water-vapor under various pressures and may embrace the interval  $+70$  to  $102^{\circ}$  C.; they may also have an auxiliary scale near the zero-point. To prevent as much as possible any changes in these thermometers when used for some time on scientific expeditions, they should be subjected to an artificial aging process (*cf.* paragraph 4) before they are sent in.

Tests will be made for every  $4^{\circ}$ , at least, or in case a millimeter scale is used, for every 50 mm. The errors should not exceed  $0.1^{\circ}$  C. or 3 mm. respectively. If an auxiliary scale be attached at  $0^{\circ}$ , the depression of the freezing-point will be determined after the thermometer has been heated for half an hour to  $100^{\circ}$ ; it should not amount to more than  $0.1^{\circ}$  C. If, however, an auxiliary scale is not attached, the depression of one of the lowest points of the scale will be determined.

14. The testing of *thermometers for technical purposes*, because of the multiplicity of their forms and the unusually large

dimensions of some of them, can be undertaken only as the facilities at hand permit.

The limits of error for these thermometers may be double those given in paragraph 12.

Thermometers made of glass free from thermal hysteresis up to  $100^{\circ}\text{C}$ . whose errors are all less than  $0.05^{\circ}\text{C}$ . are termed free from error. The number of points on the scale that will be tested is fixed according to the regulations given in the same paragraph, unless the thermometers be uncommonly long.

In the case of long technical thermometers the capillary connecting the bulb and scale must be so fine that the indications of the thermometer will not be appreciably affected by the temperature of the neck, due regard being given to the degree of accuracy required of such thermometers. If tests are to be made at higher temperatures on factory thermometers having long necks whose volume cannot otherwise be reliably ascertained, they must be sent in before they are filled under pressure so that the volume of the connecting capillary can be determined.

15. *Has to do with the limits of error, etc., of clinical thermometers.*

16. *Treats of limits of error, etc., of household thermometers.*

#### IV. CERTIFICATES, CHARGES AND TIME REQUIRED FOR TESTING.

17. Thermometers with which certificates are given will be marked to show that they have been tested by the Physikalisch-Technische Reichsanstalt with the Imperial Eagle (*Reichsadler*) and P T R, and to show that the testing has been done at Ilmenau, with the Imperial Eagle and G S.

They are also marked with a number, with which *all* thermometers with the exception of such clinical thermometers as have been found unsuitable for testing are provided.

In addition, the year is given for all thermometers listed in paragraph 1, under *a*, *b*, *c*, and *d*.

Besides the thermometric errors, the certificate contains indications, when necessary, as to the kind and application of the thermometer in question.

The rounding-off of the thermometric errors found by the tests depends upon the nature of the scale and the results of the

testing, except where a special procedure is prescribed for the individual classes of thermometers in the foregoing regulations.

As a rule the errors observed are given for the thermometers in a vertical position and with the *whole* of the liquid column immersed in the bath.

If the use of the thermometer requires the liquid column to emerge from the bath whose temperature is to be measured, information must be given when the thermometer is sent in, as to how deep the thermometer must dip into the bath and what the temperature of the emergent column may be assumed to be.

18. *Charges for testing.*

19. Thermometers will be tested in the order of their receipt as shown by the post-mark; the preliminary tests will be made at once upon the receipt of the thermometer. The tests will be finished in from three to four weeks according to their nature and the amount of work on hand.

APPENDIX.

20. *Recommendations as to the packing and sending of thermometers.*

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 19.]

A NEW SYNTHESIS IN THE QUINAZOLINE GROUP.<sup>1</sup>

(PRELIMINARY ANNOUNCEMENT.)

BY MARSTON TAYLOR BOGERT AND AUGUST HENRY GOTTHELF.

Received February 15, 1900.

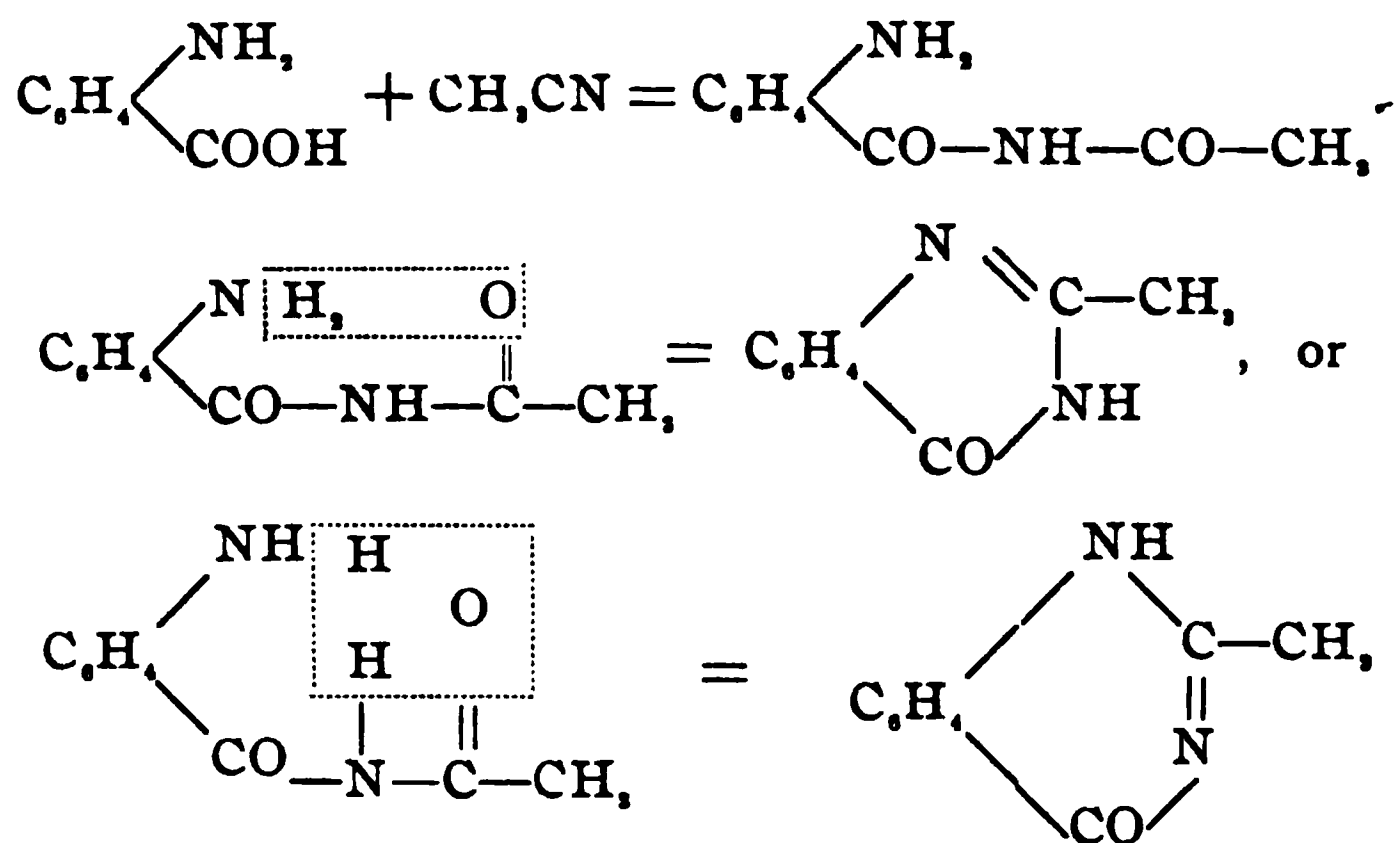
IN the course of some researches carried on in this laboratory by J. A. Mathews on "The Action of Nitriles upon Aromatic Acids,"<sup>2</sup> it was discovered that when anthranilic acid and acetonitrile were heated together in a sealed tube for five hours at 220°–230° C., instead of obtaining orthoamidobenzonitrile as expected, there resulted a crystalline product melting at 232°. This body was boiled with strong hydrochloric acid, and the solution on cooling deposited long needles which sublimed at about 280° without melting. Not enough of the substance, however, was secured for an analysis, and hence its nature could not be determined.

<sup>1</sup> Read before the New York Section, February 9, 1900.

<sup>2</sup> This Journal, 20, 654.

The writers have continued this investigation, and, by varying the conditions slightly, have readily obtained very fair yields of this substance and identified it as the 2-methyl-4-ketodihydroquinazoline first described by Weddige<sup>1</sup> and later obtained by Bischler and Burkart,<sup>2</sup> Bischler and Lang,<sup>3</sup> and Niementowski.<sup>4</sup> The needles obtained by Mathews by the action of hydrochloric acid were, of course, only the HCl salt.

The reaction by which the quinazoline compound is produced from anthranilic acid and acetonitrile is easily explained when it is remembered that, under conditions of heat and pressure, a nitrile tends to combine with an organic acid to form a secondary amide, as shown first by Gautier,<sup>5</sup> and later, in this laboratory, confirmed by the work of Colby and Dodge.<sup>6</sup> The reaction, therefore, probably takes the following course :



As early as 1860, Griess and Leibius<sup>7</sup> studied the action of cyanogen gas upon the amidobenzoic acids, and in 1869, Griess<sup>8</sup> obtained condensation products by passing cyanogen gas into aqueous and alcoholic solutions of anthranilic acid. The condensation products, however, were due entirely to a preliminary

<sup>1</sup> *J. prakt. Chem.* (2), 31, 124.

<sup>2</sup> *Ber. d. chem. Ges.*, 26, 1350.

<sup>3</sup> *Ibid.*, 28, 282.

<sup>4</sup> *J. prakt. Chem.* (2), 51, 564; and *Ber. d. chem. Ges.*, 29, 1360.

<sup>5</sup> *Ztschr. Chem.* (1869), 127.

<sup>6</sup> *Am. Chem. J.*, 13, 1.

<sup>7</sup> *Ann. Chem.* (Liebig), 113, 332.

<sup>8</sup> *Ber. d. chem. Ges.*, 2, 415.

amidine union between the cyanogen and amido groups, which in our synthesis is very improbable, both on account of the less acid character of the nitriles employed and also because Bernthsen has shown<sup>1</sup> that benzonitrile and aniline have no appreciable action upon each other even at 360° C. The products obtained would also be far different from those which we have separated.

The reaction of Niementowski,<sup>2</sup> by which he obtains quinazoline derivatives through the interaction of an amide upon anthranilic acid, appears to be a simultaneous condensation between the amido and carbonyl groups of the amide and the carboxyl and amido groups of the anthranilic acid, and is, possibly, in its internal mechanism, somewhat related to the nitrile synthesis under discussion. Niementowski found, however, that while the yield with formamide and acetamide was excellent, as the molecular weight of the amide increased it became less and less satisfactory, the higher temperature required producing more and more decomposition, and consequently more by-products, while with benzamide the condensation failed entirely and no quinazoline body could be obtained.

With our synthesis, on the other hand, using nitriles instead of amides, the reaction proceeds just as smoothly with aromatic nitriles as with aliphatic; the contents of the tubes are invariably crystalline and free from by-products (except a small amount of carbonaceous material), and by treating with boneblack and crystallizing twice from alcohol, the quinazoline body is obtained pure. We have thus prepared with the greatest ease the following derivatives of the 4-ketodihydroquinazoline, together with many of their salts:

*2-Methyl*.—Identical with that described by Weddige.<sup>3</sup>

*2-Ethyl*.—Already described by Bischler and Lang,<sup>4</sup> and by Niementowski.<sup>5</sup>

*2-Phenyl*.—Isomeric with, but not the same as the phenyl derivative of Körner,<sup>6</sup> the isomerism probably being due to a different position of the double bond in the miazine nucleus (at (1), instead of (2) ?).

<sup>1</sup> *Ann. Chem.* (Liebig), 184, 349, foot-note.

<sup>2</sup> *J. prakt. Chem.* (2), 51, 564.

<sup>3</sup> *Ibid.* (2), 31, 124.

<sup>4</sup> *Ber. d. chem. Ges.*, 28, 284.

<sup>5</sup> *J. prakt. Chem.* (2), 51, 568.

<sup>6</sup> *Ibid.* (2), 36, 155.

*2-Benzyl*.—New.

*2-Paratolyl*.—New.

The description of these bodies and their derivatives, together with many others upon which we are now at work, will be presented later. So much work has been and is being done upon quinazolines that we have deemed it wise, before entering upon the very extensive field which this new synthesis opens up, to present this preliminary notice, that we may be left free to continue our work without fear of molestation.

We should like, therefore, to reserve for the Organic Laboratory of Columbia University, the study of the action of cyanogen compounds upon organic acids, as we shall endeavor to extend this research to bodies of the aliphatic series (in the hope of obtaining oxypyrimidine compounds), as well as to other classes of compounds. We are also investigating the action of nitriles upon other ortho-substituted acids, etc., and upon closely related bodies.

When one considers the ease with which the nitriles can be obtained, especially in the aromatic series, and the fact that all the nitriles used so far, both aliphatic and aromatic, react with the same facility, it does not seem too much to say that this new process appears likely to prove the most widely applicable and most important synthesis for quinazoline compounds yet discovered.

ORGANIC LABORATORY, HAVEMEYER HALL,  
COLUMBIA UNIVERSITY, February 1, 1900.

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## A COMPARISON OF SOME FORMALDEHYDE TESTS.<sup>1</sup>

BY B. M. PILHASHY.

Received February 5, 1900.

HAVING had occasion to make some qualitative tests to show the presence of formaldehyde, I reviewed the recent chemistry for the detection of formaldehyde. In some instances the reaction given for formaldehyde proved to be true for other aldehydes also and apparently for distilled water. In some cases the delicacy of the reaction given for a particular reagent was not true for the stated dilution, while in others the reaction was clear and not to be doubted. The following summary of

<sup>1</sup> Read before the Cincinnati Section, November 15, 1899.

various reactions for the more common aldehydes may prove useful to others, who may have occasion to work in the same line.

(a) *Schiff's Reagent*.—Most aldehydes in dilute solutions give a violet coloration with this reagent. (Fuchsin decolorized by sulphurous acid.) This can also be obtained by mere exposure of the reagent to the air or by warming the suspected liquid with the reagent even in the absence of an aldehyde.<sup>1</sup>

(b) *Phenol and Sulphuric Acid*.—Most aldehydes give with very dilute phenol and sulphuric acid added to form a layer beneath, a scarlet ring changing to dark red on heating.<sup>2</sup>

(c) *Diazobenzenesulphonic Acid*.—Most aldehydes with this reagent in the presence of free alkali and sodium amalgam give an intense violet color at once or within twenty minutes. The colors are destroyed by exposure or by acid.<sup>3</sup>

(d) *Nessler's Solution*.—Acetaldehyde as well as formaldehyde gives a precipitate with Nessler's solution. They also give a precipitate with anilin.<sup>4</sup>

(e) *Dimethylanilin and Sulphuric Acid*.—Trillat gives the following reaction for formaldehyde alone. To a dilute solution a few drops of sulphuric acid and also of dimethylanilin are added. The mixture is heated for half an hour on a water-bath, made alkaline and further heated to drive off the excess of dimethylanilin which can be detected by its odor. The liquid is then filtered and the paper moistened with acetic acid. If formaldehyde is present, a blue coloration results when lead dioxide is then sprinkled on the paper.<sup>5</sup>

The following experiments tend to show that this reaction is due to dimethylanilin present.

*Experiment 1*.—If a piece of filter-paper be moistened with a very dilute solution of dimethylanilin in water it will give the blue color reaction with lead dioxide and acetic acid.

*Experiment 2*.—Twenty cc. distilled water, 2 drops of sulphuric acid, and 1 drop of dimethylanilin were mixed, forming

<sup>1</sup> Allen's "Commercial Organic Analysis," Vol. I, 3rd edition, p. 217.

<sup>2</sup> *Ibid.*

<sup>3</sup> *Ibid.*

<sup>4</sup> *Ibid.*

<sup>5</sup> *Ibid.*, p. 220.

a very dilute acid solution. This was heated one-half hour, during which time 100 cc. distilled water were added at intervals to replace that evaporated. After heating a while a strip of filter-paper dipped into this solution gave a yellow color with lead dioxide and acetic acid. Another strip dipped into the solution and made alkaline with ammonium hydroxide or sodium carbonate solution gave a slight blue after ten minutes. At the end of the heating these reactions could not be again obtained pointing to a probable volatilization of the salt formed.

*Experiment 3.*—Instead of the distilled water in Experiment 2, 20 cc. formaldehyde solution (1 : 1000) were used. After heating for one-half hour a strip of filter-paper moistened with the solution gave the yellow color observed in Experiment 2, with the lead peroxide and acetic acid and the blue color with the same reagents after making alkaline. The outside of the dish was coated with a yellow salt which was washed into a dish, made alkaline and filtered. The filter-paper gave the before-mentioned blue reaction.

*Experiment 4.*—A few drops of dimethylanilin were dissolved in water with the aid of a few drops of sulphuric acid. A strip of paper moistened with it gave the yellow reaction with lead peroxide and acetic acid. The solution was neutralized and filtered. The filter-paper as well as a strip moistened with the solution gave the blue coloration as above.

*Experiment 5.*—Twenty cc. formaldehyde solution (1 : 1000), 2 drops of sulphuric acid, and 1 drop of dimethylanilin were heated for one-half hour, made alkaline with sodium hydroxide solution and then heated for one hour longer to drive off any free dimethylanilin in excess. There was no odor to the solution which was filtered. The filter-paper gave no blue coloration with lead peroxide and acetic acid.

#### SUMMARY.

From the foregoing experiments it seems that Trillat's test does not show the presence of formaldehyde, but of dimethylanilin or its salts when not completely volatilized.



(f) *Lebbin's Test*.<sup>1</sup>—This is said to be delicate enough to detect 1 part formaldehyde in 10,000,000 of water. In my experience 1 in 200,000 seems to be the limit.

(g) *Morphin hydrochloride*<sup>2</sup> with sulphuric acid is not to be considered sensitive enough for formaldehyde in a more than 1 : 1000 solution, a purple ring being obtained.

(h) *Phenylhydrazin hydrochloride*<sup>3</sup> seems to be the best reagent for formaldehyde. The solution of 1 gram of phenylhydrazin hydrochloride with 1.5 grams sodium acetate in 10 cc. water is used. To 1 cc. of the liquid 2 drops of the reagent and 2 drops of sulphuric acid are added producing a green coloration. In as dilute a solution as 1 : 10,000 or 1 : 100,000, 3 cc. of the liquid with 4 drops of the reagent and 4 drops of sulphuric acid heated for half a minute bring out the color. For 1 : 250,000, 3 cc. of the liquid with 5 drops of the reagent and 5 drops of sulphuric acid heated for about a minute, give a very light tinge of green after three minutes, a decided tint after ten minutes.

(i) Rimini<sup>4</sup> uses *phenylhydrazin hydrochloride with sodium nitroprusside and concentrated sodium hydroxide*, a blue coloration resulting. One part in 1,000 and 1 in 10,000 give an intense blue when 1 cc. of the solution is mixed with 2 drops each of phenylhydrazin hydrochloride solution and of sodium nitroprusside solution, 1 cc. of caustic soda solution being then added. One in 100,000 gives a deep blue, and one in 1,000,000 gives a light blue. These blues change quickly to green, yellow, light brown, and red. A peculiarity is the rise of the red color to the top leaving a yellow layer below. Both layers are clear solutions. If the same amount of reagent as given above be added to dilutions greater than 1 in 1,000,000, about the same shade of blue is obtained for them,—hence the limit seems to be 1 in 1,000,000.

<sup>1</sup> Allen's "Commercial Organic Analysis," Vol. I, 3rd edition, p. 220.

<sup>2</sup> *J. Soc. Chem. Ind.*, Abst., p. 955 (1898).

<sup>3</sup> *Ibid.*, p. 954.

<sup>4</sup> *Ibid.*, p. 697.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA  
UNIVERSITY, No. 20.]

## SOME NEW TELLURIUM COMPOUNDS.

BY VICTOR LENHER.

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**I**N many points tellurium resembles selenium in its derivatives, the oxides are not unlike in their behavior, and the tellurites and tellurates are very similar to the corresponding selenites and selenates.

Tellurium, owing to its high atomic weight, shows greater stability in its higher halogen derivatives than the preceding members of the group to which it belongs. Two series of halides are known, corresponding to  $\text{TeX}_2$  and  $\text{TeX}_4$ . The tetrahalides are those most commonly met with and seem to be the type which tellurium tends to follow with the halogens. With selenium, on the contrary, we find the lower halides are the more stable. Heat transforms the tetra- into the monohalides with corresponding loss of halogen.

As in the case of the other natural groups of elements, the basic property is found to increase with the rise in atomic weight, so here also we find the same tendency in the higher members to be more basic than the lower ones. Sulphur is a decidedly acid element; in selenium this property is decidedly weaker, while with tellurium we actually find such salts as the tartrate, basic sulphate, and basic nitrate, which are not known in the case of a true non-metal. In appearance, tellurium resembles a metal, while sulphur and selenium, in the elementary condition, certainly do not appear metallic.

As a result of this increase in basic properties, we should expect to find that tellurium forms better defined double halides than selenium. This is actually the case. Only the double bromides of selenium are known. Attempts to prepare double chlorides thus far have proved unsuccessful, and likewise the formation of double bromides of selenium is restricted within certain limits.

It has been shown by the author<sup>1</sup> that selenium tetrabromide can unite with the hydrobromides of the organic amines to form

<sup>1</sup> This Journal, 20, 572.

well-defined double salts in which the amine plays the rôle of ammonia in the compound  $(\text{NH}_4)_2\text{SeBr}_4$ . Norris<sup>1</sup> has also prepared a number of the double halides of selenium.

When tellurium replaces selenium in the double halides, we obtain more clearly defined compounds than is the case with the latter. In fact, while selenium tetrabromide unites with only the hydrobromides of the fatty amines and with the hydrobromides of pyridine and piperidine, no compound could be prepared with any of the true aromatic amines or with quinoline; neither has it been possible to prepare an aromatic or aliphatic amine salt in which selenium tetrachloride replaces the tetrabromide.

Both tellurium tetrabromide and tetrachloride form a series of beautiful salts with the aliphatic amines, and both of the halides also unite with the aromatic amines to form well-defined derivatives. In the series of salts which has been prepared, it is somewhat striking to notice that all the bromides are red while the chlorides are invariably yellow. Wheeler<sup>2</sup> has shown that the double chlorides of tellurium with potassium, rubidium, and cesium are yellow while the corresponding bromides are red.

To prepare the salts it is only necessary to add a solution of tellurium dioxide in hydrochloric or hydrobromic acid to the amine salt dissolved in the corresponding acid; a precipitate of the double salt generally forms immediately, and this precipitate, when recrystallized from dilute acid, gives crystals of the salt in a purified condition.

All the double salts are decomposed by pure water with the formation of hydrated  $\text{TeO}_2$ , but are soluble in dilute acids and in alcohol.

*Method of Analysis.*—Great difficulty was at first experienced in making an analysis of these compounds, owing to the complications which invariably ensued. The method which was finally adopted consisted in dissolving a weighed quantity of the salt in a dilute solution of tartaric acid, adding to this a measured excess of standard silver nitrate and a few drops of ferric alum. The solution was then treated with a standard solution of ammonium thiocyanate. The object of the tartaric acid was

<sup>1</sup> *Am. Chem. J.*, 20, 490.

<sup>2</sup> *Ztschr. anorg. Chem.*, 3, 428.

to hold in solution the tellurium dioxide, which otherwise would be precipitated by the water, and to prevent the formation of a precipitate of silver tellurite which would interfere with the titration. When a sufficient quantity of tartaric acid is present to hold tellurium dioxide in solution and prevent its action on the silver, the method proves very accurate. The silver nitrate solution was made up of such strength that 1 cc. = 0.007969 gram bromine or 0.003533 gram chlorine.

*Methylamine Bromotellurate*,  $(\text{CH}_3\text{NH}_2)_3\text{TeBr}_6$ .—To a solution of methylamine in hydrobromic acid, a hydrobromic acid solution of  $\text{TeO}_2$  was added, when a red precipitate immediately formed. This was collected on a filter and the salt purified by recrystallization from dilute hydrobromic acid.

0.3023 gram salt required 27.1 cc. silver nitrate solution.

	Calculated for $(\text{CH}_3\text{NH}_2)_3\text{TeBr}_6$ .	Found.
Br .....	71.50	71.44

The crystals are of a red color and are regular octahedrons, having a high index of refraction.

*Methylamine Chlorotellurate*,  $(\text{CH}_3\text{NH}_2)_3\text{TeCl}_6$ .—This substance was prepared in a manner similar to the preceding; that is, a hydrochloric acid solution of tellurium dioxide was added to a solution of the amine in hydrochloric acid and the product recrystallized from dilute hydrochloric acid.

0.3029 gram salt required 44.9 cc. silver nitrate solution.

	Calculated for $(\text{CH}_3\text{NH}_2)_3\text{TeCl}_6$ .	Found.
Cl .....	52.67	52.37

The crystals appear as yellow hexagonal plates, with a micaceous cleavage. The index of refraction is low, and in polarized light a low order of colors is shown.

*Ethylamine Bromotellurate*,  $(\text{C}_2\text{H}_5\text{NH}_2)_3\text{TeBr}_6$ .—Exactly the same procedure was adopted in the preparation of this salt as with the methylamine derivative.

0.3056 gram salt required 26.3 cc. silver nitrate solution.

	Calculated for $(\text{C}_2\text{H}_5\text{NH}_2)_3\text{TeBr}_6$ .	Found.
Br .....	68.63	68.58

The crystals are red hexagonal plates which show a strong

basal cleavage. In polarized light the colors are of a low order, and the refractive index is fairly high.

*Ethylamine Chlorotellurate*,  $(C_2H_5NH_2)_3TeCl_6$ .—This salt forms yellow hexagonal plates showing a strong cleavage, and in polarized light showing a low order of colors.

0.3034 gram salt required 42.1 cc. silver nitrate solution.

	Calculated for $(C_2H_5NH_2)_3TeCl_6$ .	Found.
Cl.....	49.24	49.02

*Trimethylamine Bromotellurate*,  $[(CH_3)_3NH]_3TeCl_6$ .—This salt is the most strongly crystalline of all the compounds prepared. It forms red orthorhombic crystals which have a fairly high index of refraction. The crystals show a low order of colors in polarized light, but in convergent light a biaxial figure is readily seen.

0.3029 gram salt required 24.9 cc. silver nitrate solution.

	Calculated for $[(CH_3)_3NH]_3TeBr_6$ .	Found.
Br.....	65.98	65.51

*Aniline Bromotellurate*,  $(C_6H_5NH_2)_3TeBr_6$ .—The action of the bromide of tellurium on aniline hydrobromide is quite unlike that of selenium tetrabromide. In the case of selenium, no compound seems to be formed, the aniline actually reducing the bromide of selenium even in acid solution.

When a solution of tellurium dioxide in hydrobromic acid is added to aniline hydrobromide, a red precipitate forms, which can be purified by recrystallization from dilute hydrobromic acid. The salt then appears as red monoclinic tablets which act strongly on polarized light.

0.3053 gram salt required 23.3 cc. silver nitrate solution.

	Calculated for $(C_6H_5NH_2)_3TeBr_6$ .	Found.
Br.....	60.34	60.82

*Aniline Chlorotellurate*,  $(C_6H_5NH_2)_3TeCl_6$ .—While selenium tetrabromide does not enter into combination with aniline hydrobromide, tellurium tetrabromide as has been seen, readily forms a double salt. The formation of double chlorides with selenium remains yet to be shown, while here we have the first example of the union of tellurium tetrachloride with the salt of an aro-

matic amine. This salt, which was prepared in a manner similar to the preceding is, like all of the chlorides, yellow in color. The crystals of the salt were too small to determine their form, but they are active to polarized light. The salt is very light and feathery.

0.3017 gram salt required 34.2 cc. silver nitrate solution.

	Calculated for (C <sub>5</sub> H <sub>5</sub> NH <sub>2</sub> ) <sub>2</sub> TeCl <sub>6</sub> .	Found.
Cl .....	40.25	40.04

*Pyridine Bromotellurate*, (C<sub>5</sub>H<sub>5</sub>NH),TeBr<sub>6</sub>.—This compound forms fine red crystals, not large enough to determine the crystallographic system of the salt, but it was found to be active to polarized light.

0.3041 gram salt required 24.1 cc. silver nitrate solution.

	Calculated for (C <sub>5</sub> H <sub>5</sub> NH),TeBr <sub>6</sub> .	Found.
Br .....	62.55	63.15

*Pyridine Chlorotellurate*, (C<sub>5</sub>H<sub>5</sub>NH),TeCl<sub>6</sub>.—This salt forms yellow isometric crystals having a low index of refraction. The crystals were very small.

0.3012 gram salt required 36.2 cc. silver nitrate solution.

	Calculated for. (C <sub>5</sub> H <sub>5</sub> NH),TeCl <sub>6</sub> .	Found.
Cl .....	42.54	42.46

*Quinoline Bromotellurate*, (C<sub>9</sub>H<sub>7</sub>NH),TeBr<sub>6</sub>.—Very small red crystals of the salt were obtained, which were found to act on polarized light.

0.3026 gram salt required 21.00 cc. silver nitrate solution.

	Calculated for (C <sub>9</sub> H <sub>7</sub> NH),TeBr <sub>6</sub> .	Found.
Br .....	55.32	55.30

*Quinoline Chlorotellurate*, (C<sub>9</sub>H<sub>7</sub>NH),TeCl<sub>6</sub>.—The crystals of this salt were also very small and were active to polarized light.

0.3051 gram salt required 30.6 cc. silver nitrate solution.

	Calculated for (C <sub>9</sub> H <sub>7</sub> NH),TeCl <sub>6</sub> .	Found.
Cl .....	35.44	35.43

It thus appears that both the tetrachloride and tetrabromide of tellurium readily form double salts with the salts of both the fatty and the aromatic amines. The salts crystallize well,

and their color seems to be dependent on the halogen content, the bromides being invariably red, and the chlorides yellow.

A solution of tellurium dioxide in halogen acids gives a precipitate with nearly all of the alkaloids, probably forming salts similar to those above described. The alkaloid derivatives are now being studied in this laboratory.

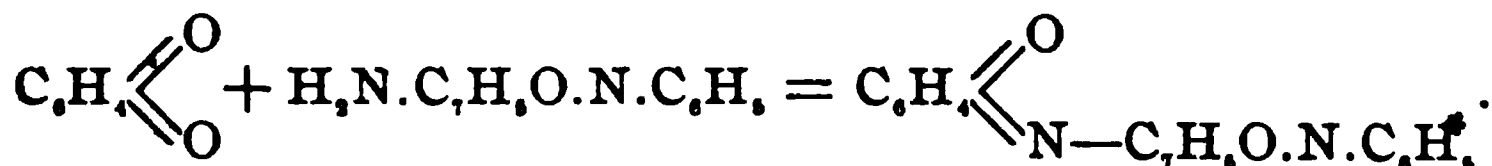
## THE ACTION OF $\alpha$ -ACYLATED PHENYLHYDRAZINES ON THE CHLORINE DERIVATIVES OF QUINONES.

(PRELIMINARY REPORT.)

BY WILLIAM MCPHERSON AND ROBERT FISCHER.

Received January 29, 1900.

THE investigations of Zincke<sup>1</sup> on the interaction of phenylhydrazine and the quinones led to the general result that  $\alpha$ -naphthoquinone,  $\beta$ -naphthoquinone, and phenanthraquinone condense in a normal manner with phenylhydrazine, but that under similar conditions, all of the quinones of the benzene series give hydroquinones, the reaction being attended with gas evolution. Many subsequent efforts have been made to effect a normal condensation between benzoquinone and phenylhydrazine, since this reaction would help to solve the problem of the constitution of the oxyazo-bodies. Although this has not as yet been accomplished, it has been shown by one of us<sup>2</sup> that the unsymmetrical acylated phenylhydrazines, *e. g.*,  $C_6H_5N.C_7H_5O.NH_2$ , condense with benzoquinone in a normal manner forming a hydrazone derivative in accordance with the following equation :

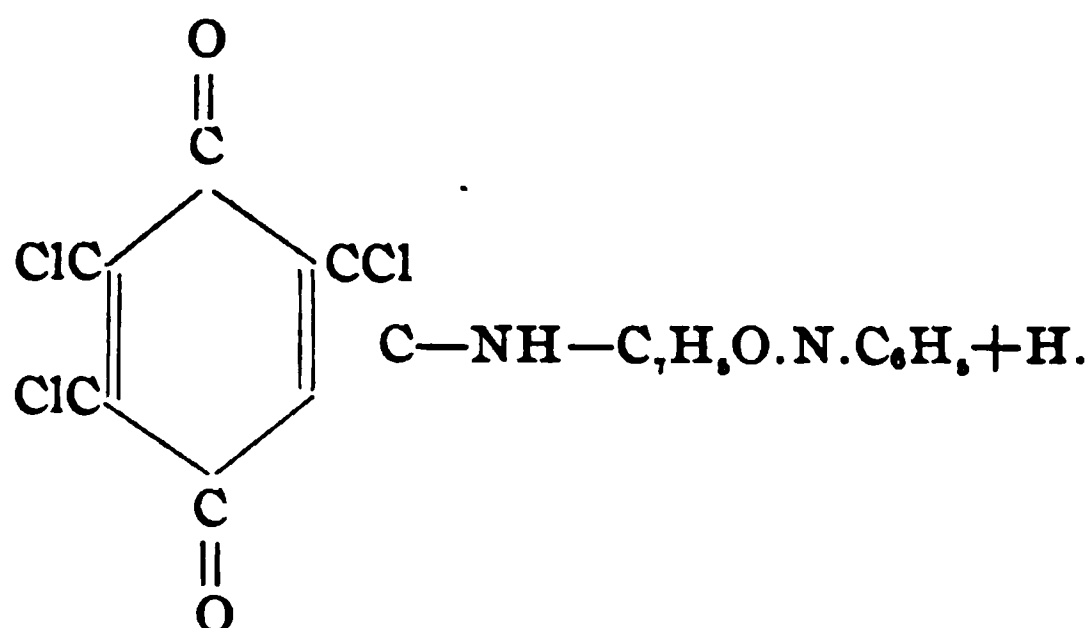
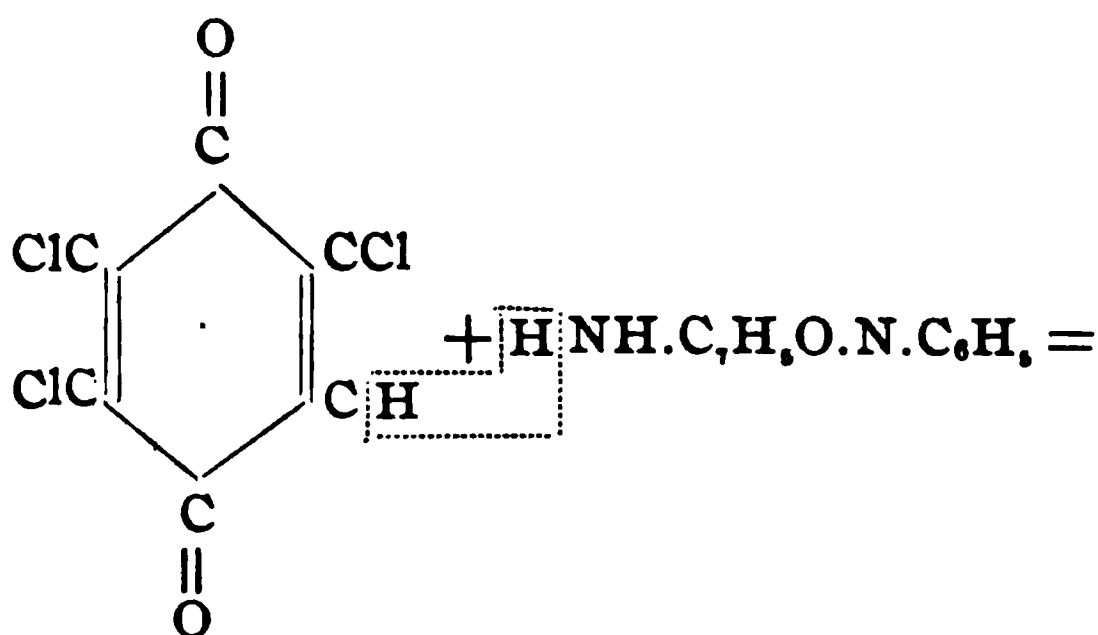


This reaction has recently been extended to the chlorine derivatives of quinone. It has been found, however, that while the  $\alpha$ -acylphenylhydrazines react with these readily, the compounds formed are not hydrazones but *hydrazino* derivatives, possessing a structure similar to the so-called anilidoquinones, formed by the interaction of quinones and aniline under certain conditions. With trichlorbenzoquinone the following reaction

<sup>1</sup> *Ber. d. chem. Ges.*, 16, 1563.

<sup>2</sup> *Ibid.*, 28, 2414; *Am. Chem. J.*, 22, 364.

takes place, the two hydrogen atoms being removed by the oxidizing action of a second molecule of the quinone.



This reaction is analogous to the interaction of trichlorquinone and aniline, investigated by Niemeyer,<sup>1</sup> the point of attack being the hydrogen of the quinone in preference to the chlorine.

Tetrachlorquinone gives with  $\alpha$ -benzoyl phenylhydrazine the same product as trichlorquinone, hydrochloric acid being evolved.

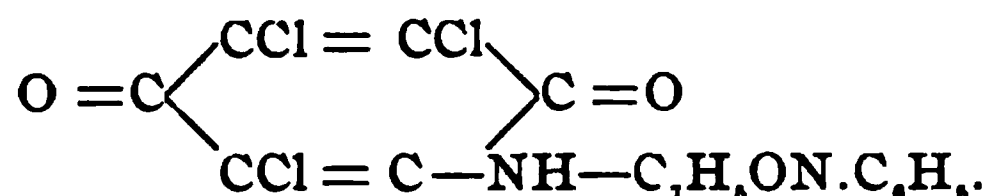
It is quite probable that under different conditions, hydrazone derivatives of the chlorquinones may be obtained. This subject is now under investigation in this laboratory. The interaction of the quinones and the unsymmetrical naphthylhydrazine derivatives is also being studied with the hope of isolating both the true oxyazo-bodies and their isomeric quinonehydrazones and thus definitely deciding the constitution of the so-called free oxyazo-bodies.

<sup>1</sup> *Ann. Chem.* (Liebig), 228, 322.



## EXPERIMENTAL PART.

*Action of  $\alpha$ -Benzoyl Phenylhydrazine on Trichlorbenzoquinone.*—  
 $\alpha$ -Benzoyl phenylhydrazino trichlorquinone,



The hydrazine was prepared according to Widman's excellent method,<sup>1</sup> for the preparation of unsymmetrical hydrazines. Some slight changes in the process were found advantageous. In the case of  $\alpha$ -benzoyl- $\beta$ -acetylphenylhydrazine the following method easily gives the pure solid product, in place of the difficultly solidifying oil which Widman first obtained. To 10 grams of pure  $\beta$ -acetylphenylhydrazine were added 70 grams of benzene and 9.4 grams of benzoyl chloride. The flask was connected with a return condenser and its contents heated to boiling. The hydrazine slowly dissolved with evolution of hydrochloric acid. After heating for a few minutes the  $\alpha$ -benzoyl- $\beta$ -acetylphenylhydrazine began to separate on the sides of the flask owing to the slight solubility of the body in benzene. After heating for one hour, the reaction was complete. On cooling, the product was removed by filtration, and was obtained pure (m. p. 152°–153°) by a single crystallization from alcohol diluted with an equal volume of water. The yield is nearly quantitative. From this the difficultly soluble sulphate  $(\text{C}_6\text{H}_5\text{.NC}_6\text{H}_5\text{O.NH}_2)_2\text{H}_2\text{SO}_4$  was prepared by saponification as directed by Widman. In the first experiments the free base was obtained from this sulphate and then converted into the soluble hydrochloride. In the later experiments, however, it was found advantageous to use the original sulphate, dissolving it in water to which was added just enough alcohol to effect solution.

Four grams of trichlorquinone and 7 grams of  $\alpha$ -benzoylphenylhydrazine sulphate in a finely divided condition were placed in a flask and 300 cc. of water, 140 cc. of alcohol, and a few drops of sulphuric acid added. The flask was connected with a return condenser and the contents boiled for five minutes. The red powder which separated was then filtered from the hot liquid and dried on a clay plate (yield 5 to 6 grams). The body was

<sup>1</sup> Monograph "Ueber asymmetrische Secundäre Phenylhydrazine," published by the "Gesellschaft der Wissenschaften" at Upsala 1893; also *Ber. d. chem. Ges.*, 26, 945.

easily purified by crystallizing from benzene, or from benzene-ligroin. Melting-point  $158.5^{\circ}$ .

1. 0.1641 gram substance gave 0.1668 gram silver chloride.
2. 0.2115 gram substance gave 0.2127 gram silver chloride.
1. 0.2397 gram substance gave 0.4714 gram carbon dioxide and 0.0620 gram water.
2. 0.2484 gram substance gave 0.4891 gram carbon dioxide and 0.0619 gram water.

	Calculated for $C_{11}H_{11}N_2O_2Cl_2$ .	Found.	
		1.	2.
C .....	54.09	53.63	53.69
H .....	2.63	2.87	2.76
Cl .....	25.23	25.13	24.86

$\alpha$ -Benzoyl phenylhydrazino trichlorquinone is a bright red crystalline body, readily soluble in hot benzene and alcohol, from each of which it crystallizes in long rectangular prisms or in star-shaped groups of small prisms. It is sparingly soluble in ligroin, and practically insoluble in glacial acetic acid and dilute caustic soda solution. Its action with phenylhydrazine is similar to that of quinone, decomposition occurring with evolution of gas. By dissolving in concentrated sulphuric acid as well as by the action of alcoholic potash, the benzoyl group is split off, but some further reaction takes place forming a dark brown crystalline body. This is soluble in caustic soda and melts with decomposition at  $198^{\circ}$ . Its structure has not yet been determined.

OHIO STATE UNIVERSITY, January, 1900.

## NOTE ON A METHOD OF STANDARDIZING WEIGHTS.

BY THEODORE WILLIAM RICHARDS.

Received February 26, 1900.

ALTHOUGH nowadays it is possible to procure, for a comparatively small sum, sets of weights which are reasonably exact, it is recognized that for gravimetric work demanding any considerable degree of accuracy, corrections on account of occasional errors in the weights must be applied. It is obvious, moreover, that if the relative values of the weights in an inexpensive box are known, this set may serve a purpose which would otherwise demand a much more expensive one. For ten years every student in quantitative analysis at Harvard has been required to standardize his weights; and since the method

adopted has some peculiarities, not described in the usual directions for this purpose,<sup>1</sup> it is explained below. This method does not pretend to be especially original ; the reason for its publication is simply a desire to advance the cause of accuracy.

According to our method the weights to be standardized are weighed wholly on one side of the balance, the comparison being made by substitution. This procedure, of course, eliminates a possible inequality in the length of the arms of the balance, which must otherwise be computed. A more important advantage is the fact that it also obviates the mental confusion resulting from the continual interchanging of weights between the opposite pans. Thus is avoided one of the common sources of error in the beginner's work.

It is, of course, necessary that all of the fractional weights should, taken together, constitute a gram ; and because the milligram weights are never used, it is convenient to add an extra centigram weight from another set to supplement the other small weights. The different weights of the same denomination should be marked in a recognizable way, and should always be arranged in the same order in the box. The comparison usually begins with centigrams and proceeds upwards. One of the centigram weights is placed upon the *left-hand* scale-pan, and is balanced by any suitable tare, care being taken that the rider is not too near either end of its path.<sup>2</sup> The zero point of the balance need not have been taken in the first place. The swings of the balance with its centigram load are now carefully noted and then another centigram weight is substituted for the first. Obviously, the amount by which the rider must be moved to attain the same position of equilibrium gives at once the difference between the two weights ; and even the neophyte could hardly err as to its sign. Of course, instead of moving the rider, the difference may be calculated from the change in the swings ; or both swings and rider may be used. The first weight is then replaced upon

<sup>1</sup> For the usual method adopted by Kohlrausch, see Ostwald's Handbook of Phys. Chem. Measurements (Walker), p. 41.

<sup>2</sup> A crude set of weights is, of course, the most convenient tare, and a 5 milligram weight may be kept on the left-hand pan so that the rider may assume a convenient position. The use of the *left-hand* scale-pan for the weights to be standardized renders a confusion of the sign of the correction less likely, because the rider is on the right. In this case, the *weights are the objects to be weighed*, and hence naturally take the left-hand position.

the left-hand pan, and if the swings correspond to the first observation it is reasonably certain that the balance has remained in a constant condition throughout the trial, and hence that the difference between the two weights has been accurately determined. In this way every weight is compared with every other weight of the same denomination, as well as with the combination of all the smaller weights. Thus are obtained a number of independent equations one less than the number of weights; and by assuming the value of any one of the weights the others may all be calculated.<sup>1</sup>

We have found it most convenient for the purposes of calculation to make the temporary assumption that the first centigram weight is correct. From it by the simplest possible process of addition and subtraction may be built up quickly the values of all the other weights. While the values thus computed are wholly consistent among themselves, they are usually far too different from the face values of the weights for convenient use. The reason of this is because the assumed standard is so small a quantity. It is necessary then to translate these consistent values into other terms by dividing every value by the value of one of the larger weights, to be taken as the new and permanent standard.<sup>2</sup>

This division (which would demand six or seven place logarithm tables for the larger weights) is conveniently replaced, however, by a simple method depending upon the properties of small numbers in presence of large ones.<sup>3</sup> It is quite sufficiently accurate to compare the value of each weight with the corresponding aliquot part of the value of the weight to be taken as a final standard. The difference between the actual value and the ideal value will give at once the correction to be applied to the weight.

<sup>1</sup> Of course, many extra equations, which are not independent of the others, are obtained by the literal fulfilment of the preceding directions. These extra equations may be used to verify the final results, if desired. The comparisons best suited for the calculation are given in a table on a following page.

<sup>2</sup> If it is desired to refer the whole box of weights to the international standard, it is, of course, necessary to include a weight which has been standardized at Washington in the series, and thus to find the value of the international gram in terms of the centigram chosen as the temporary basis. The aliquot parts or multiples of this value are then used precisely in the manner indicated further on. For all ordinary purposes, however, this is wholly unnecessary; and one of the 10-gram pieces of the box is a more convenient standard.

<sup>3</sup> Nernst und Schoenflies Math. Behand. der Naturwiss, p. 303 (1895).

Of course, if the weight is not heavy enough this correction carries a *minus* sign, and must be *subtracted* from the result of any weighing in which that weight is used; for the deficiency necessitates the addition of extra weight on the rider-arm, and hence the sum of the face-values of all the weights used is too large. Long experience has shown that the sign of the final correction is the most insidious cause of error in the whole process; for the beginner always thinks that if a given weight is too light, its correction should be *added*.

The table below presents all the data and results of a sample standardization, as well as all the calculation which need be written down by anyone possessing even a moderate ability to add figures mentally. In the first column the weights are named by their face-values, which are enclosed in parentheses in order to show that they do not signify true grams. In the second column are given the results of the mutual comparison of these weights copied from a note-book in which every detail of each weighing was recorded. The third column gives the actual values of the weights based upon the first centigram weight; these values are obtained by simply adding together the appropriate preceding values in the third column and the last minute fractional weight enumerated in the second column. The aliquot parts of the value for the 10-gram piece, which is now to be taken as the permanent standard, are recorded in the fourth column, while the corrections sought, obtained by simply subtracting the numbers in the fourth column from those in the third, are given in the last vertical row.

Nominal values.	Data obtained by substitution method. Grams.	Preliminary val- ues (actual). Grams.	Aliquot parts of 10.01768 (ideal). Grams.	Corrections in mil- ligrams (actual minus ideal). <sup>1</sup>
(0.01) = Standard of comparison		Standard	0.01002	—0.02
(0.01') = (0.01)	+ 0.00006	0.01006	0.01002	+0.04
(0.01'') = (0.01')	— 0.00001	0.01005	0.01002	+0.03

<sup>1</sup> Owing to neglected fractions the figures in the last column, when added together, are sometimes slightly discordant with those given in the second column. This is inevitable; of course such corrections should always be calculated to one decimal place beyond the figure which one wishes to have exact.

Nominal values.		Data obtained by substitution method. Grams.	Preliminary values (actual). Grams.	Aliquot parts of 10.01768 (ideal). Grams.	Corrections in milligrams (actual minus ideal). <sup>1</sup>
(0.02)	=	(0.01) + (0.01') - 0.00001	0.02005	0.02004	+0.01
(0.05)	=	(0.02) + etc. --0.00007	0.05009	0.05009	±0.00
(0.1)	=	(0.05) + etc. --0.00006	0.10019	0.10018	+0.01
(0.1')	=	(0.1) +0.00001	0.10020	0.10018	+0.02
(0.2)	=	(0.1) + (0.1') - 0.00004	0.20035	0.20035	±0.00
(0.5)	=	(0.2) + etc. --0.00011	0.50088	0.50088	±0.00
(1)	=	(0.5) + etc. --0.00004	1.00183	1.00177	+0.06
(1')	=	(1) - 0.00002	1.00181	1.00177	+0.04
(1'')	=	(1) - 0.00006	1.00177	1.00177	±0.00
(2)	=	(1') + (1'') +0.00025	2.00383	2.00354	+0.29
(5)	=	(2) + etc. --0.00040	5.00884	5.00884	±0.00
(10)	=	(5) + etc. --0.00040	10.01768	10.01768	Standard.
		etc.	etc.	etc.	etc.

It is convenient to prepare from the individual corrections a card exhibiting at once the corrections corresponding to the usual combinations of weights from 1 to 99 centigrams and from 1 gram upwards. This card minimizes both the labor of applying the corrections and the danger of possible error in the process. It is hardly worth while to print here an example of such a card, but the method of application may be illustrated. The page of the note-book is ruled with two parallel vertical lines, which contain the two corrections found in the card. The upper correction corresponds in each case to the whole grams, and the lower to the fractional weights.

	Observed weight. Grams.	Cor. mg.	Corrected weight. Grams.
Weight of crucible + substance .	19.3105	{ +0.39 } { -0.01 }	19.3109
“ “ “ alone.....	16.9916	{ +0.06 } { +0.06 }	16.9917
Weight of substance .....	.....		2.3192

Thus the increased accuracy is gained with very little sacrifice of time or mental labor. It is usually more convenient to adjust the rider by filing to exactly 12.0 (or 10.0) milligrams rather than to apply a correction for this also.

<sup>1</sup> See foot-note, p. 147.

The method of comparing the actual value with an ideal one is also a convenience in standardizing burettes by means of the Ostwald "calibrator." In the original description of this process it is assumed that the calibrator delivers exactly an integral number of cubic centimeters;<sup>1</sup> but if only a few instruments are to be calibrated it is both troublesome and expensive to secure such a precise instrument. We have found it convenient to use a calibrator of any size, and to compare in parallel columns its multiples with the actual readings of the burette. The capacity of this calibrator is most conveniently obtained in the following manner. Suppose that as a mean of several comparisons it has been found that sixteen fillings of the calibrator correspond to 49.53 cc. on a given burette. Grease is the most serious foe to accuracy in this process. The burette is now refilled, and exactly this amount of pure water is run out into a weighed flask, with all the precautions which would be used in an actual titration. The weight of the water gives by appropriate calculation<sup>2</sup> the true volume of sixteen fillings of the calibrator. Suppose this was found to be 49.44 cc.; then the volume of the calibrator as it is actually used in a calibration must be  $\frac{49.44}{16} =$

3.090 cc. The differences between the successive readings of the burette and the successive numbers 3.09, 6.18, 9.27, . . . etc., give at once the errors of the graduation of the tube at these intervals. These differences or corrections may be plotted on a diagram in which the ordinates are volumes and the abscissas corrections. The correction to be applied for 50 cc. is obviously -0.09 cc. Here again the sign is somewhat perplexing to the inexperienced.

These simple methods have stood the test of years of use in our first course upon quantitative analysis, and their practicability under these circumstances shows that reasonable accuracy in weights and measures is within the easy reach of all.

HARVARD UNIVERSITY, CAMBRIDGE, MASS.,  
February 20, 1900.

<sup>1</sup> Ostwald: Handbook of Phys. Chem. Measurements (Walker), p. 87 (1894).

<sup>2</sup> This Journal, 21, 527 (1899).

## METHODS FOR THE DETECTION OF "PROCESS" OR "RENOVATED" BUTTER.

BY W. H. HESS AND R. E. DOOLITTLE.

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'**P**ROCESS" butter commonly called "renovated" butter is a product prepared about as follows: Unsalable dairy or creamery butter, bought at a low price in the spring and summer, is melted and the butter-fat drawn off. The curd originally present in the butter is rejected, thereby removing a large part of the rancidity if any be present. Milk is now added to this butter-fat and stirred in so as to be evenly mixed throughout, when the whole mass is cooled quickly, so as to prevent the separation of the "butter oil." This milk soon sours, the casein therein is coagulated, and thus there is provided an artificial curd which contains a percentage of nitrogen about the same as that of the curd of real dairy butter. The butter-fat of this renovated butter does not materially differ from ordinary butter-fat in any of its chemical properties.

It is evident, therefore, that for the detection of process butter, we must depend on the difference between the curd of genuine butter made from cream, and the artificial curd supplied in "process" butter by the addition of milk. There are proteids in milk which are insoluble in water, and therefore separate out and occur with the cream. The insolubility of these proteids was more fully brought out by S. W. Babcock in his work upon the proteids of cream (1888). These proteids, insoluble in water, pass into the butter and form the main part of the substance commonly known as the curd. It is a cohesive, gelatinous mass and notably non-granular. The curd of "process" butter, however, consists chiefly of coagulated casein. This is a flaky, granular, non-cohesive mass, and does not, therefore, resemble the proteids of cream in physical properties. The following method of analysis has proved satisfactory :

### TEST FOR BUTTER-FAT.

The purified fat is examined with the butyro-refractometer. At 25° C., the reading seldom varies from 51° in the case of "process" butter, and hence does not differ from butter-fat in



this respect. This reading is taken to assure the operator that the fat at hand is butter-fat and not a substitute, as oleomargarine. A determination of the volatile fat acids will serve as well.

#### **TESTS OF THE CURD.**

After having proved that the fat is butter-fat, an examination of the curd is made. The first test that is made is one which depends on the cohesive properties of the curd of pure butter. If a portion of the butter sample, about 1 gram, is placed in a convenient container—a spoon answers the purpose admirably—and heated over a free flame, the mass will, in case the sample is pure butter, assume a foamy appearance, which is very striking. In case the sample is “process” butter, no foaming is produced, but the mass merely bumps and sputters like hot grease containing water. Oleomargarine behaves like “process” butter, but it has been excluded by previous tests.

#### **APPEARANCE OF THE CURD.**

A sample of the butter is melted in a beaker, the fat is decanted, and the curd is well washed with ether to remove the remnant of fat. The curd is poured out on a clean glass plate in a thin layer and allowed to dry. A sample of genuine butter is treated likewise. The physical appearance is then quite distinctive especially when a magnifier of 3 to 6 diameters is used for the examination. The curd from the true butter will have an amorphous, non-granular appearance, while the curd from “process” butter has a very coarse, curdy appearance. The one is the proteid of cream, the other is the proteid of milk; the one is a gelatinous, ropy mass, the other is a granular, easily divided substance. Casein dissolves readily in acid or alkali; the curd of genuine butter dissolves only on prolonged treatment with these reagents.

#### **IDENTIFICATION OF THE SOURCE OF THE CURD.**

A convenient sample of the butter, 25 to 100 grams, is placed in a beaker and melted at 45° to 50° C. (It is worthy of note that “process” butter will not yield a clear liquid fat at the end of half an hour or even twenty-four to forty-eight hours, while genuine dairy or creamery butter yields a clear supernatant liquid as soon as melted.) As much as possible of the fat is

decanted, and the remaining portions, composed of curd, water, salt, and the remnant of fat, are thrown upon a moistened filter and the water is allowed to drain through. This water carries the soluble proteids as well as salt. To this filtrate, a few drops of acetic acid are added and then the solution is brought to a boil. In case the filtrate is from the curd of pure butter, only a slight milkiness is produced (absence of albumins); but in case the filtrate is from the curd of "process" butter a flocculent, white precipitate of albumins is formed, a certain indication that the source of the curd is from milk. Other tests for the albumins may, of course, be used. If strong hydrochloric acid be added to the filtrate from the curd of "process" butter, a violet color is produced (Liebermann's test for albumin).

#### QUANTITATIVE EXAMINATION OF THE CURD.

If the artificial curd of "process" butter has been derived from milk, then the ratio of the percentage of casein to the percentage of albumins should be the same as that ratio is in milk, or about 9 parts of casein to 1 part of albumins. The ratio in the curd of "process" butter sold on the market, as actually found, was 8.6 parts of casein to 1 part of albumins. The method of estimation is as follows: 50 grams of the butter are placed in a beaker and dissolved in ether to a clear solution. In case the sample is genuine butter, the curd is so finely divided that it remains in suspension in the ether and considerable time may be required for a clear solution. As much as possible of the ether solution of fat is decanted and the whole of the remainder transferred to a separatory funnel. The casein and water with the salt are then removed and the washing with ether repeated three or more times to remove all the fat from the curd. The casein is then filtered out, washed with water, and the nitrogen estimated by the Kjeldahl method. The filtrate from the curd is made slightly acid with acetic acid and then brought to a boil. The albumins are filtered out and estimated by the same method.

These tests serve to differentiate between genuine butter and "process" butter, as it is now found on the market.

# CHEMICAL METHODS FOR ASCERTAINING THE LIME REQUIREMENT OF SOILS.

By H. J. WHEELER, B. L. HARTWELL, AND C. L. SARGENT.

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HAVING recognized the occurrence of an injurious degree of acidity in the upland soils of Rhode Island and other states, even upon steep hillsides, it became important to ascertain by chemical means if possible the relative lime requirement of different soils. If such could be done in a simple and effective way, then one would be in a position to recommend satisfactorily what amount of lime to use per acre without resort to field tests.

## TESTS BY BLUE LITMUS PAPER.

Perhaps the simplest, though nevertheless a very satisfactory test, is that made by bringing a piece of blue litmus paper in contact with the moistened soil and observing the intensity and rapidity of the reddening thus produced. Though unsatisfactory, in view of its not being a quantitative test, much valuable information regarding the amounts of lime which should probably be used, may thus be obtained, after some experience, by one who is a careful observer. Wahnschaffe<sup>1</sup> in speaking of this reaction says, "since the free carbonic acid of the soil reddens the paper, one must allow it to dry and observe whether or not the red color is still visible." Roscoe and Schorlemmer<sup>2</sup> state that "carbonic acid readily decomposes into water and carbon dioxide. In consequence of this, litmus paper which has been turned red in the aqueous acid, becomes blue on drying." They then immediately add that the reddening of litmus solution may be brought about by conducting into it carbon dioxide, but that upon heating the solution the carbon dioxide is expelled, and after boiling a few seconds the liquid again becomes blue. In Watts' Dictionary of Chemistry<sup>3</sup> it is stated that an "aqueous solution of CO<sub>2</sub> turns blue litmus paper wine-red ; the blue color returns on exposure to air." It seems probable that on account of the well-known reaction of litmus solution whereby, when reddened by carbon dioxide gas, it returns to a blue color, it has

<sup>1</sup> Anleitung zur wissenschaftlichen Bodenuntersuchungen, Berlin (1887), p. 56.

<sup>2</sup> "Treatise on Chemistry," I, New York (1888), p. 638.

<sup>3</sup> Vol. I, London (1890), p. 695.

been assumed that a similar reaction would necessarily take place when operating with litmus paper. This conclusion seems exceedingly probable since the writers have been unable to find references in the literature to any definite tests bearing upon this point. It is possible also that tests, if made, were carried out by operating with carbonic acid upon small sections of a piece of litmus paper, in which case, sufficient alkali might diffuse from the surrounding paper into the section acted upon, to neutralize the carbonic acid still remaining. That such a return of the blue color may result when the entire portion of the litmus paper is not subjected to treatment with acid, has been demonstrated by us upon commercial paper in the case of carbonic acid and of very dilute citric acid.

Owing to the action of the fingers upon blue litmus paper and the bleaching action of the sun, the test would be far simpler and more reliable in the hands of practical farmers if it were not necessary to wait for the paper to dry before drawing conclusions as to the probable needs of the soil. In view of the fact that some of the conditions prevailing when working with litmus paper are so different from those existing when employing the solution, it seemed probable that blue litmus paper, if entirely reddened by carbonic acid, and dried with the promptness that would ordinarily be expected, would not return to its original blue color. Dr. H. E. Stockbridge told one of us that he was under the impression that he once found this to be the case. In order to test this matter thoroughly, trials were made with ordinary commercial blue litmus paper and also with lots of paper prepared from solutions made according to Classen<sup>1</sup> and Sutton.<sup>2</sup> The carbonic acid was prepared by expelling the carbon dioxide from an aqueous solution of chemically pure sodium bicarbonate by simply boiling without the use of acid. A return condenser was employed and the carbon dioxide was washed in distilled water before its collection. Steam, generated from the distilled water which was used subsequently to dissolve the sodium bicarbonate, was first passed through the entire apparatus for some time and the distillate tested to insure the absence of

<sup>1</sup> Böckmann's "Chemisch-technische Untersuchungsmethoden", Vol. I, Berlin (1888), p. 97.

<sup>2</sup> The third method. Sutton's "Handbook of Volumetric Analysis", London (1882), p. 31.

volatile organic acids. Treated with carbonic acid prepared in this way all three lots of blue litmus paper were permanently reddened when dried naturally in the open air or in a room free from acids and ammonia. It is evident therefore that when dried naturally the carbon dioxide is not lost to any great extent or else the red, acid coloring-matter of the litmus is too firmly fixed upon the fiber of the paper, to permit of its reunion with the base, a change which would have resulted in the case of a solution, after the expulsion of the carbon dioxide. Coupling with these results the fact that so long as a liberal amount of calcium carbonate is present in a soil, the presence of carbonic acid tends to increase rather than lessen the tendency toward an alkaline reaction<sup>1</sup> (a point proved by us experimentally in the laboratory) it must be evident that the indication of acidity afforded by a piece of blue litmus paper is sufficient to show a deficiency of calcium carbonate or other basic ingredients in soils, without first allowing the paper to dry, as suggested by Wahnschaffe.

#### TESTS BY EXTRACTION WITH AMMONIA.

Müntz<sup>2</sup> states that it is easy to distinguish whether or not a soil is acid, since if such is the case it imparts a black color to ammonium hydroxide when the two are brought in contact. He adds that in the case of soils which are not acid, the organic matter is in an insoluble combination with lime and consequently yields nothing to ammonium hydroxide. The same has been found by us to be the case with a sample of fertile adobe soil kindly forwarded by Professor Goss, from New Mexico. Similar observations have also been made on one Massachusetts and two Rhode Island soils where wood ashes or calcium carbonate in some form had been applied to the land with such frequency as to entirely overcome its acid reaction upon blue litmus paper. Snyder,<sup>3</sup> however, calls attention to a soil which he says contained 3.15 per cent. of lime (CaO) and 4.19 per cent. of carbon dioxide, and yet when treated with ammonium hydroxide for the determination of the so-called "free humic acid" yielded a dark brown extract amounting to from 0.3 to 0.4 of a

<sup>1</sup> Compare Detmer Die naturwissenschaftlichen Grundlagen d. allg. landw. Bodenkunde (1876), p. 451; also Stöckhardt, Jahrbuch für Agriculturchemie (1866), p. 10.

<sup>2</sup> Encyclopédie Chimique, 4, Pt. 4, p. 18.

<sup>3</sup> Bulletin No. 56, Chemical Division, United States Department of Agriculture, Washington, D. C., 1899.

per cent. This would tend to throw some doubt upon the reliability of the treatment with ammonium hydroxide as a means of arriving at the lime requirements of all soils, though it is not improbable that for soils of certain sections of the United States which are possessed of definite characteristics, the treatment may be of considerable value as was the case in the particular acid soils, for which Müntz employed the method. The details of the method as proposed by Müntz<sup>1</sup> are as follows: To 20 grams of powdered soil, add 50 cc. of concentrated ammonium hydroxide. Allow it to stand for from two to three days in a warm place. Agitate frequently and at the end of the period make the volume up to 1 liter. It is then shaken and allowed to subside for twenty-four hours. To 500 cc. of the liquid add sufficient hydrochloric acid to give a strong acid reaction in order to precipitate the humus, which carries with it some mineral matter. After the precipitate has subsided, decant the supernatant liquid, collect on a filter, dry and weigh in a weighing bottle, incinerate, deduct the ash, and the "free humic acids" are thus obtained by difference. In order to determine what influence, if any, the use of concentrated ammonium hydroxide might have upon the results compared with dilute solutions, a sample of upland soil was tested by the above method and yielded 1.00 per cent. Treated for the same time with the same amount of ammonium hydroxide previously diluted to 500 cc. (containing 1.13 per cent. of ammonia) it also yielded 1.00 per cent. The same soil treated for a like time with 500 cc. of the same solvent containing 2.4 per cent. of ammonia yielded 1.00 per cent. Employing sufficient concentrated ammonium hydroxide so that after diluting to 500 cc. it would have the same strength as in the last-mentioned instance, it yielded, treated for the same time, 1.03 per cent. It appears therefore that in the case of ordinary soils the strength of the solvent within reasonable limits is not an essential feature, and that the solution usually employed in total humus determinations may be used here with equal propriety.

#### THE METHOD OF HOLLEMAN FOR DETERMINING THE LIME REQUIREMENTS OF STIFF CLAY SOILS.

Holleman<sup>2</sup> in searching for the cause of the occasional

<sup>1</sup> Encyclopédie Chimique, 4, Pt. 4, p. 182.

<sup>2</sup> Die landw. Versuchs-stationen 41 (1892), p. 38.

ineffectiveness of gas-lime upon certain stiff clays in Holland concluded that it might be due to the presence in them of considerable calcium carbonate. He thereupon made determinations of the lime removable by water and by water saturated with carbon dioxide. The water-soluble lime was determined as follows: Twenty grams of air-dried soil were digested with frequent shaking, at ordinary temperature, for forty-eight hours with 1 liter of distilled water. Five hundred grams of the filtrate to which a few drops of acetic acid had been added were evaporated, the residue taken up in water; and first a little acetic acid and then a measured quantity of  $\frac{N}{10}$  solution of ammonium oxalate were added and the volume made up to 100 cc. After filtration, the excess of oxalic acid is estimated by titrating with a  $\frac{N}{10}$  solution of potassium permanganate. For determining the lime soluble in carbonic acid 20 grams of air-dried soil are taken and sufficient distilled water added to make up 1 liter; it is then saturated with carbon dioxide and after twenty-four hours filtered and treated as described above. From the data obtained by Holleman, he concluded that where extraction with carbonic acid removed 0.15 per cent., or less, of calcium oxide, stiff clay soils would be benefited by liming.

In order to test the applicability of this method to the acid sandy and clayey loam soils of our State, two samples were selected, the first being from a farm in Warren, R. I., where, with the same manurial and other treatment, the yield of beets upon the unlimed plot was 272 pounds against 329 pounds upon the limed plot. The second soil was from Foster Center, R. I., where under the same conditions the yield of beets upon the unlimed plot had been 36.6 pounds and upon the limed one 143.4 pounds. In making the test of the soil from Warren, 80 grams of soil were employed, and in that from Foster Center, 40 grams. The soil was placed in each case in a flask to which 1 liter of distilled water, saturated with carbon dioxide, was added. The flask was agitated frequently and the treatment continued for forty hours. Four hundred cc. of the extract were evaporated to dryness, taken up in water and a little acetic acid,  $\frac{N}{10}$  ammonium oxalate was added, and after filtration, the whole was made up to 200 cc. Aliquot parts of this solution were titrated with  $\frac{N}{10}$  potassium permanganate, after acidulation with sulphuric acid. In

one instance the small amount of acetic acid was removed by evaporation to dryness before adding sulphuric acid and titrating without practically affecting the results. Allowing for the blank found, the amount of calcium oxide thus determined amounted in the Foster Center soil to 0.0360 per cent. In the case of the Warren soil, which was treated in the same manner, the amount of calcium oxide removed from the soil was found to be 0.0287.

The Warren soil extracted with distilled water, in a similar manner for forty-eight hours, yielded 0.0120 per cent. of calcium oxide.

From these tests it will be seen that the soil which was least benefited by lime, yielded less lime than the other. It is possible that the use of double the amount of soil in the last instance may have depressed the result somewhat as compared with the other, though it is not likely that the difference caused by this factor would, under the circumstances, have been readily appreciable. At all events the amount of lime removed in the highest case was only about one-fifth of that below which Holleman found lime useful on stiff clays.

It appears, therefore, in view of the marked degree of acidity of those of our soils which it seemed desirable to test as to their lime requirements, that this method is probably not of great value. It is regretted, nevertheless, that the pressure of routine work has prevented making further tests of the applicability of the method to our special needs, particularly with greater attention to maintaining the saturation of the carbonated water.

#### THE METHOD OF TACKE FOR DETERMINING THE FREE HUMUS ACIDS IN THE PEAT (MOORBODEN) SOILS OF NORTH GERMANY.

Tacke<sup>1</sup> states that no method is known for determining quantitatively the acidity of soils, and calls attention to the desirability of possessing a satisfactorily exact method for the purpose. He discusses the difficulties in the way of determining the acidity by various ways which would naturally suggest themselves, and finally gives a method which yielded good results. It is impossible to give the method satisfactorily in

<sup>1</sup> *Chem. Ztg.*, No. 20, 1897, p. 174.



detail without reproducing the illustration of the apparatus which he employed. Essentially the method consists in expelling the carbon dioxide from calcium carbonate brought in contact with the soil at ordinary room temperature. Hydrogen is passed over the soil for some time in the apparatus, then finely divided calcium carbonate, shaken up with water, is introduced and allowed to act upon the soil for two and a half hours or longer as desired. The carbon dioxide disengaged is taken as a measure of the acidity of the soil, the amount being determined by passing it through a Pettenkofer tube containing  $\frac{N}{5}$  or  $\frac{N}{10}$  sodium hydroxide. The liquid is finally removed from the tube, taking care in regard to the absorption of carbon dioxide from the air, barium chloride then added and the solution titrated with  $\frac{N}{5}$  or  $\frac{N}{10}$  hydrochloric acid using phenolphthaleïn as an indicator with attention to the points brought out by the investigations by Küster<sup>1</sup> and by Lunge.<sup>2</sup> Determined in this way, using soil in its natural state, the amount of acid reckoned as carbonic acid, represented by 100 parts of dry material, amounted in the case of various peat soils to from 1.721 to 2.240 per cent. The method gives promise of much value for such soils as a guide to the amount of lime which they should receive. In April, 1895, experiments were begun by one of us for the purpose of ascertaining if the amount of carbon dioxide liberated from calcium carbonate upon heating it with upland acid soils in the presence of water, could be used as a guide to the amount of lime to apply to them. Owing to the pressure of routine matters, this work was several times taken up and then soon discontinued. Not having satisfactorily perfected a method at the time Tacke's results were published, it was decided to see if his method was applicable to our upland soils. Two unlimed soils were selected for the trial, the one from land where sodium nitrate had been applied for several years and the other from land where the manuring had been identical except that the same quantity of nitrogen had been applied in ammonium sulphate. The yields of most crops had been for several years far better upon the former than upon the latter plot of land.

<sup>1</sup> *Chem. Ztg. Repert.*, 29, 282 (1896); *Ztschr. anorg. Chem.*, 13, 127 pp. (1896).

<sup>2</sup> Bestimmung von Caustischen und Kohlensauren Alkalien, G. Lunge, *Ztschr. angew. Chem.*, 41 (1897).

The percentage of carbon dioxide obtained by treatment for three hours, calculated to dry soil, was 0.039 for the soil which had received sodium nitrate and 0.067 for the one which had received ammonium sulphate. In other words the results stood in the same relation as the yields. Taking into account the fact that the soils contained nearly 4 per cent. of humus and from 1.25 to 1.55 per cent. of humus immediately soluble in ammonium hydroxide, it is evident that the action of this class of soils upon calcium carbonate, at ordinary temperature, is far less vigorous than that of the peat soils tested by Tacke. The percentages obtained by this method are so small, and the element of error proportionately so great, that the indications are not particularly favorable to its use with soils of the character to which it was hoped the test would apply.

#### DETERMINATION OF TOTAL HUMUS.

The determination of total humus could only be expected to throw light upon the lime requirement of soils where marked acidity of the soil exists, and while it might even then bear no relation to the benefit to be derived from liming, it was deemed of interest to ascertain by actual tests what relation, if any, would be found. Combined with the tests to determine the amount of humus soluble in ammonium hydroxide, without previous extraction of the soil with hydrochloric acid, it was also possible to learn if there appeared to be any relation between the gain from liming and the percentage of the total humus, which was directly soluble in ammonium hydroxide.

The method employed was essentially that of Grandeau as modified by Huston and McBride.<sup>1</sup> Twenty grams of soil were first extracted with hydrochloric acid as proposed by Hilgard<sup>2</sup> with the employment of an automatic washing apparatus, until no further reaction for lime was obtainable in the wash solution. After the removal of the acid by successive washings with distilled water, the material was extracted with ammonium hydroxide, aliquot portions of the extract evaporated to dryness, incinerated, the ash deducted and the humus thus obtained by difference. The relation between the results obtained and the data

<sup>1</sup> Wiley's "Principles and Practice of Agricultural Analysis," Vol. I, 327, 328.

<sup>2</sup> *Ibid.*, p. 325.

secured in actual experiments with lime upon several soils will be discussed later.

DETERMINATION OF THE AMOUNT OF LIME REMOVABLE BY  
HYDROCHLORIC ACID.

In soils containing some calcium carbonate, a number of methods have been proposed for arriving at their probable need of lime. Among others, Mondesir<sup>1</sup> gives a method by which he proposes to ascertain the active calcium carbonate in soils, since, as he says, soils may contain considerable of this substance, perhaps so surrounded by particles of clay that for practical purposes it is of little or no use, and nevertheless stand in need of lime. In our own soils which have been shown to contain practically no calcium carbonate, it must be evident that such methods can be of no avail. If the need of lime, in soils of the character under consideration, is determinable by the quantity of lime present, regardless of its form, then extraction with a strong mineral acid ought to serve as a fair basis for arriving at the lime requirement of the soil. Various methods of treatment, with different kinds, strengths, and volumes of acids have been proposed. For the purpose in hand the method<sup>2</sup> of the Association of Official Agricultural Chemists of the United States was followed, the digestion of the soil (10 grams) having been carried on for ten hours with 100 cc. hydrochloric acid (1.115 sp. gr.) at the temperature of boiling water with the employment of a return condenser. The data thus secured, with soils tested in a practical way with lime, in the field, are given later in tabular form in which connection they will be discussed.

ACIDITY BY TITRATION.

If means could be devised for determining the relative acidity, or the lime requirements of soils by titration, the matter would be rendered extremely simple and the tests could be made in great numbers at small expense. Owing to the extreme insolubility of the acids, or acid compounds of the soil, the titration of a watery extract of the soil could not be expected to furnish any very valuable data. In order to obtain, if possible, results which might indicate in some measure the probable affinity for lime

<sup>1</sup> *Annales de la Science Agron.*, 2, 270 (1887).

<sup>2</sup> *Bull.* 46, Div. of Chemistry, U. S. Dept. of Agriculture, pp. 39, 40.

(the substance which would usually be applied in the neutralization of soils), a study was made of the action of lime-water, the strength of the supernatant liquid, after contact with the soil for some time, being determined by titration. Air-dried soil was employed so as to eliminate any possible influence which might arise from drying at higher temperatures. Owing to the fact that these trials were only preliminary, and on account of the slight variation in the moisture of the soils examined which varied but little from 2.25 per cent., no correction has been applied to the results for the moisture contained in the soil itself. Ten grams of air-dried soil were brought in contact with 50 cc. of lime-water in a small flask. The flask was securely corked and occasionally agitated. At the end of about twenty hours the supernatant liquid was passed rapidly through a dry filter, an excess of hydrochloric acid of known strength (3 cc. neutralizing 36.1 cc. of the lime-water) added and the amount of unneutralized acid determined by titration with lime-water. In this way the volume of lime-water neutralized by 10 grams of the air-dried soil was indirectly determined. With the same soil more lime-water was required, without exception, where it had remained unlimed, than where lime had been applied. In the comparison of two unlimed soils manured alike excepting that one had received its nitrogen for several years in sodium nitrate and the other in ammonium sulphate, the differences in the amounts of lime-water neutralized were not always in harmony with, nor were they marked enough to accord at all with the experience obtained in tests of the soils made by plants themselves. In a comparison of limed and unlimed soils it was found that by employing a greater amount of lime-water (75 cc.) greater differences were obtained than by the use of but 50 cc. Possibly the use of even a somewhat greater amount would have given even better comparative results. Trials were also made, employing hydrochloric acid twenty times as dilute as that first tried. Coralline was used as an indicator, and though far from satisfactory in some respects, it was the only one tried which proved at all effective.

The preliminary trials not having indicated any particular general value of such a method, a trial of ammonium hydroxide was next made.

## TITRATION TESTS BY MEANS OF AMMONIUM HYDROXIDE.

A number of preliminary tests gave indications that the use of ammonium hydroxide in place of lime-water, was capable of giving results more nearly in accord with those obtained by plant tests. The method finally used was as follows: Fifteen grams of air-dried soil were placed in a glass flask and 100 cc. of about  $\frac{N}{10}$  ammonium hydroxide and 100 cc. of distilled water added. This was allowed to stand at the ordinary temperature of the laboratory for about forty-two hours, with frequent agitation during the earlier portion of the time. After it had finally been allowed to settle, a definite amount of the supernatant liquid was treated with hydrochloric acid (about  $\frac{N}{2}$ ) at the rate of five cc. for each 20 cc. of the liquid, and made up to a given volume. After the precipitated humus had subsided, aliquot portions of the solution (50 cc.) were titrated with ammonium hydroxide, using coralline as an indicator. Since by this treatment some portion of the organic acids may be dissolved by the ammonia, the method cannot give an absolute idea of the acidity of a soil. On the other hand, a method which determines the humus immediately soluble in ammonium hydroxide before extraction with hydrochloric or other strong acid, gives no indication of the acidity represented by acid inorganic compounds. Possibly if the amount of humus soluble in ammonium hydroxide were determined, and likewise the amount of ammonia held at the same time in combination by the insoluble residue, the combined data might furnish a better guide than either one alone. Unfortunately the occasional opportunities available for conducting such investigations have not yet permitted a study of this question.

In order to ascertain what effect a variation in the strength and volume of the ammonium hydroxide and the volume of soil might have, a given<sup>1</sup> soil was tested in various ways.

(1) Twenty grams of soil were treated with 100 cc. of ammonium hydroxide diluted with a like quantity of water.

(2) Twenty grams of soil were treated with 50 cc. of ammonium hydroxide diluted with 150 cc. of water.

<sup>1</sup> Berthelot and André (*Ann. chim. phys.*, 7th Série, 1, 286 (1894)) in operating upon organic residues from soils treated with hydrofluoric acid, state that the amount of potassium oxide held by the organic matter varied with the strength of the potassium hydroxide with which it was treated.

(3) Twenty grams of soil were treated with 200 cc. of ammonium hydroxide.

(4) Twenty grams of soil were treated with 150 cc. of ammonium hydroxide.

(5) Fifteen grams of soil were treated with 100 cc. of ammonium hydroxide.

The following were the amounts of ammonium hydroxide retained in combination by the soil calculated in each case to 10 grams of substance.

	Ammonium hydroxide. cc.
(1).....	14.3
(2).....	11.1
(3).....	13.5
(4).....	14.0
(5).....	13.7

It will be seen from a careful examination of the data that they give some indication that only the weakest solution materially affected the results.

The trials of a number of Rhode Island soils by this method as described on page 170 are given in a subsequent table where the data may be compared with those obtained by other chemical methods and with the actual gains in yield of beets, obtained by the employment of lime.

METHOD FOR DETERMINING THE LIME REQUIREMENT OF SOILS  
BY COMPARING, UNDER IDENTICAL CONDITIONS, THE COLOR  
OF AN AMMONIUM HYDROXIDE EXTRACT OF SOILS OF  
UNKNOWN CHARACTER WITH ONE OF KNOWN CHARACTER.

The method employed was to treat in a warm room like amounts of soil with like volumes of ammonium hydroxide (containing about 2.4 per cent. of ammonia) for two days with occasional agitation. The small amount of water contained in the air-dried soil itself has been shown to exert no appreciable effect upon the result so that for approximate comparisons, drying a portion of the soil at a high temperature and making allowances for the water in the soil, is unnecessary. The colors of the solutions are finally compared and if darker than the standard, they are diluted with water to match it, or if lighter in color some of the standard solution prepared from the

soil of known character, is similarly diluted until it matches the one with which the comparison is being made. The amount of dilution in either case measures the excess or deficiency of color as compared with the standard. It was thought that certain weighable matters might be extracted by ammonium hydroxide from unhumified plant residues which might not color the solution to the same extent as the matter which is actually humified. In such a case, this method might perhaps give better indications than that as employed by Müntz (see page 155). The possible variation in color of the individual ingredients of the complex, which is classed as humus, may in some cases seriously interfere with the use of the method.

The rapidity with which a large number of comparative determinations can be made after the material has settled, is a strong point in its favor as compared with the method of Müntz. The results obtained by both methods may be compared below in connection with those obtained in actual plant tests upon limed and unlimed soil.

ATTEMPTS TO DETERMINE THE LIME REQUIREMENT OF SOILS  
BY MEASURING THE CARBON DIOXIDE EXPELLED UPON  
HEATING A GIVEN QUANTITY OF SOIL, IN THE PRESENCE  
OF WATER, WITH CALCIUM CARBONATE OR WITH SODIUM  
CARBONATE.

This work was begun in April 1895, at which time Tacke's method of treating peat soils at ordinary temperatures with calcium carbonate, had not been published. No notice of similar attempts to arrive at the lime requirement of soils having been found, the line of work was apparently wholly new and had to be conducted without the aid of any previous experience.

The first soil selected for this work was from the permanent experimental plot No. 23, which had been manured annually beginning with the year 1893, with the following commercial materials ; *viz.*, dissolved bone-black, potassium chloride and ammonium sulphate. The same arrangement was employed for the absorption of the carbon dioxide as is customary in ordinary determinations of carbon. As a preliminary trial 40 grams of soil, containing 24 per cent. of water capable of being driven off at 100° C., were placed in a Wolff flask and heated, in the

presence of water, with 4 grams of calcium carbonate. On account of the rapid evolution of carbon dioxide, the heating had to be conducted with the utmost care, as the boiling-point was approached, in order that the gas might be entirely absorbed.

A blank test with a definite amount of water and 80 grams of the soil (passed through a sieve containing holes  $\frac{1}{8}$  of an inch in diameter) gave 0.0124 gram of carbon dioxide. A blank test with the water and 8 grams of calcium carbonate yielded 0.002 gram of carbon dioxide. Assuming that no carbon dioxide came from the calcium carbonate, 80 grams of the soil must have yielded upon heating in the manner described but  $(0.0124 - 0.002)$  0.0104 gram of carbon dioxide.

Eighty grams of soil were heated with the same amount of water and calcium carbonate, and kept at the boiling-point until the evolution of gas seemed to have become practically constant and but very limited in amount. The carbon dioxide yielded, amounted to 0.338 gram. Assuming again that the entire blank from the water and calcium carbonate was due to the water and deducting therefore the blank of 0.0124 gram, it is seen that the amount of carbon dioxide found to have been liberated as a result of the action of the calcium carbonate upon the 80 grams of soil, was 0.3256 gram. Owing to rapid evolution of gas on approaching the boiling-point, which necessitated the frequent removal of the lamp, it was feared that some carbon dioxide must have passed through the entire apparatus.

A subsequent test with 40 grams of soil and 8 grams of calcium carbonate was then made. Deducting a blank of 0.0052 gram for the soil and 0.002 gram for the water and calcium carbonate, the amount of carbon dioxide expelled by the soil was found to be 0.1762 gram. This corresponds to 0.3524 gram for 80 grams of soil as compared with 0.3256 gram in the first test, but in the last test great care was exercised that no carbon dioxide should be lost.

A third test with 40 grams of soil and 4 grams of calcium carbonate yielded 0.178 gram of carbon dioxide. Deducting, as above, a blank of 0.0072, the amount of carbon dioxide found to have been liberated by the soil was equivalent to 0.3416 gram for 80 grams of soil.

In order to ascertain if differences between soils corresponding



to those shown by the growth of plants could be detected, a soil (from permanent Plot No. 27) was selected which had been manured the same as the other excepting that it had received its nitrogen in sodium nitrate instead of in ammonium sulphate. A blank test with 40 grams of soil and with the usual amount of water yielded 0.015 gram of carbon dioxide. A test with 40 grams of soil gave, after deduction of the blank just mentioned, 0.1402 gram of carbon dioxide or the equivalent of 0.2804 gram for 80 grams of soil, or much less than was shown by the soil first tested. This accorded with the results secured in plant tests and indicated much greater acidity where nitrogen in ammonium sulphate had been employed than where nitrogen in sodium nitrate was used, or where a basic instead of an acid residue had been left in the soil. In all of the tests thus far made, the operation was stopped after the chief evolution of gas was apparently over and when only a constant and very slight evolution was still noticeable.

To ascertain the effect of longer heating, 40 grams of soil and 4 grams of calcium carbonate were treated for a much longer time than heretofore. The amount of calcium oxide eliminated, allowing for the blank of 0.015 gram was equivalent for 80 grams of soil to 0.3126 gram as compared with 0.2804 gram where the period of heating was less prolonged. Another test was made under the same conditions, continuing the heating for about the same period as in the preceding instance. The net amount of carbon dioxide driven off, per 80 grams of soil, amounted to 0.322 gram. The same material brought to boiling once more and heated for some time yielded, per 80 grams of soil, 0.032 gram of additional carbon dioxide. Brought to boiling and heated for a third time the further loss for the same amount of soil was equivalent to 0.0256 gram. From these tests it appeared probable that beyond a certain point the attack upon the calcium carbonate became very limited or that a gradual oxidation or else a splitting up of the organic matter was taking place. To ascertain if this would go on at an appreciable rate at ordinary temperatures, a current of air was next passed for two and one-half hours over the material which had been thus successively heated. As a result it was found that no weighable amount of carbon dioxide had been eliminated. Further heating, as

before, resulted in a still further elimination of carbon dioxide and an increase in the weight of the absorption tubes. From this it was evident that there was apparently no reasonable time limit within which the elimination of carbon dioxide would be ended, and hence to obtain satisfactory comparative tests with different soils, the period of treatment, temperature, and other conditions must all be kept as uniform as possible. One apparent drawback to the method as it was used, was the necessity of conducting the heating so cautiously, and in consequence, for so long a time, in order that the carbon dioxide might all surely be absorbed, for by doing so the opportunity for the gradual breaking up of the organic matter was much increased. To overcome this objection, in a measure, the use of soda-lime was resorted to as an absorbent for carbon dioxide. By this means, less care was required to insure the absorption of the gas and the period of heating could be materially reduced. Nevertheless the method was still unsatisfactory, and in consequence, it was proposed to operate so as to subject the material to the action of heat a minimum length of time and either measure the volume of the carbon dioxide disengaged or to determine it indirectly by titration with the employment of barium hydroxide, or by estimating the amount of carbonate formed from it and so indirectly the carbon dioxide. Preliminary to this work it was thought wise to ascertain if possible the minimum time that it was necessary to heat the calcium carbonate and soil, in the presence of water, to insure that all of the humus had united with calcium oxide. It is well known that in many cases where soil contains naturally considerable quantities of lime and magnesia, ammonium hydroxide extracts practically no humus until the lime and magnesia have first been removed by acids. Such has been found to be the case in soil from New Mexico and with certain soils from Massachusetts and Rhode Island, which had been treated successively with calcium carbonate. The idea therefore suggested itself that by heating a number of soils with calcium carbonate and water for varying intervals of time, and subsequently testing the residues with ammonium hydroxide, it could be ascertained how long it was necessary to continue the heating in order to get practically all of the humus into an insoluble combination with lime. It was thought that this time

might be safely taken as the limit for continuing the heating and that the amount of carbon dioxide thus disengaged would serve as a suitable measure of the lime requirement of soils. It was also proposed to test the method with soils which do not react acid, in order that further light might be thrown upon the probable applicability of such a method to the purpose in hand. Unfortunately, routine work has prevented the further carrying on of this investigation. It is a question of too great scientific and practical interest to be laid aside at this point, and it is hoped that opportunity for further pursuit of the question will be afforded in the near future.

COMPARISON OF THE GAIN IN BEETS, RESULTING FROM THE  
USE OF LIME, WITH THE DETERMINATION OF THE LIME  
REQUIREMENT OF SOILS MADE BY VARIOUS CHEMICAL  
METHODS.

The following table shows the amounts of beets produced upon limed and unlimed soil in different sections of Rhode Island. Each plot was manured alike with commercial nitrate of soda, muriate of potash and dissolved bone-black. The table gives the percentage gain from liming, also the amount of humus immediately soluble in ammonium hydroxide, the percentage of "total" humus, the amount of calcium oxide removable by extracting with strong mineral acid, the number of milligrams of nitrogen in the ammonia held in combination by 10 grams of soil, the comparative dilution of the ammonium hydroxide extract of a soil of known character to give a degree of coloration corresponding to that exhibited by the extracts from the different soils tested, the amount of calcium oxide removable by carbonated water and the percentage of material in the respective soils which was so coarse as not to pass a sieve with openings  $\frac{1}{16}$  of an inch in diameter. Only such material as passed circular openings of this size, was employed in the various tests.

The analytical data in the table were obtained with soil passing a sieve with hole  $\frac{1}{16}$  of an inch in diameter. The results are calculated to dry soil.

Locality.	Yield of table beets.		Percentage gain in yield (of beets) from liming.	Total humus. <sup>1</sup>	Humus immediately soluble in ammonium hydroxide. <sup>2</sup>	Percentage of the total humus which was immediately soluble in ammonium hydroxide.	Milligrams of nitrogen in the ammonia retained from ammonium hydroxide by 10 grams of soil. <sup>3</sup>	Comparative amount of dilution in volume of the ammonium hydroxide extract of the Kingston soil to make it match in color similar extracts from the other soils. <sup>4</sup>	Lime (CaO) determined by the official method of the A. O. A. C. <sup>5</sup>	Lime (CaO) soluble in carbonated water. <sup>6</sup>	Soil materials too coarse to pass a sieve with holes of an inch in diameter
	Unlimed plot.	Limed plot.									
	Pounds.	Pounds.		Per cent.	Per cent.	Per cent.			Per cent.	Per cent.	
Warren .....	27.2	32.9	21.0	2.67	0.90	33.71	21.21	3.3	0.382	0.029	7.00
Summit .....	47.4	92.9	96.0	1.73	0.84	48.55	19.61	4.0	0.386	*	22.30
Jamestown .....	75.8	152.7	101.5	0.85	0.53	62.35	10.41	5.0	0.261	*	1.15
Harrisville .....	151.5	207.3	102.8	1.46	0.42	28.77	14.09	6.6	0.429	*	11.75
Foster Center .....	36.6	143.4	291.8	2.21	0.70	31.67	25.53	2.5	0.558	0.036	6.45
Niantic .....	9.9	43.4	338.4	0.95	0.46	48.42	7.92	4.0	0.112	*	14.65
So. Portsmouth .....	26.0	153.0	488.5	2.63	0.99	37.64	27.16	2.5	0.348	*	7.25
Hamilton .....	14.5	131.8	809.0	1.60	1.02	63.75	15.76	3.0	0.281	*	3.40
Kingston Hill .....	6.6	161.4	2,345.5	5.15	1.99	38.64	36.09	0.0	0.412	*	*
Slocumville .....	1.0	101.8	10,080.0	5.08	1.41	27.76	43.77	0.3	0.553	*	1.10

\* Not determined. <sup>1</sup> See method, p. 160. <sup>2</sup> See method, p. 163. <sup>3</sup> See method, p. 164. <sup>4</sup> See method, p. 164. <sup>5</sup> See method, p. 161. <sup>6</sup> See method, p. 157.

It will be seen that in the foregoing table the Warren soil which was least helped by lime, is placed at the top, the others being arranged in the order of the benefit noted, from top to bottom, with the Slocumville soil, representing a gain of 10,080 per cent. as a result of liming, placed at the foot of the list.

Comparing the percentages of material extracted immediately by treatment with ammonium hydroxide, with the gains from liming, it will be seen that there is no regular correspondence. The tests show a successive decrease in the first three soils while the crop increased. The Niantic soil shows a similar decrease. Of these soils, those at Niantic and Jamestown were exceedingly sandy, while those at Harrisville and Summit were quite gravelly. The result with the Warren soil was unexpectedly high. In the case of the balance of the "heavier" or more compact soils, a successive increase in humus immediately soluble in ammonium hydroxide was noticed, corresponding well, with the exception of the Slocumville soil, with the crop results. In fact this was the only method tried which indicated differences between the So. Portsmouth and Hamilton soils corresponding with those afforded by the crops. It will be noted that the Slocumville soil showed more benefit from liming than that at Kingston, though the latter gave a higher test by this method than the Slocumville soil. For the heavier classes of soils containing naturally considerable quantities of humus, this method gives much promise of usefulness. In the case of the more silicious soils containing but moderate amounts of humus, the method may perhaps indicate with considerable truthfulness the relative lime requirements within the particular class, but when it comes to comparisons of individuals of the one class with those of the other, it is possible that it fails to indicate the truth with sufficient accuracy on account of a considerable amount of the acidity being due more to inorganic, than to organic matter.

In support of this, it may be cited that many of our subsoils, which contain only minimum quantities of organic matter, are decidedly acid, indicating the presence of acid silicates, or other acid inorganic compounds. Mondesir<sup>1</sup> found that upon the destruction of all of the organic matter in a soil by means of "permanganate" at a temperature below 100° C., or by combus-

<sup>1</sup> *Compt. rend.*, 115, 317, August (1892).

tion at dull red heat, and after subsequent treatment at ordinary temperature with very dilute hydrochloric or nitric acid, followed by complete removal of these by washing with distilled water and subsequent heating for several hours at from 160° to 170° C., the soil residue was still acid. It decomposed calcium carbonate to some extent at ordinary temperature, and still further upon heating with water to the boiling-point.

It is of interest to note that in the case of the Slocumville soil, where beets almost absolutely refuse to grow without the aid of lime, only 27.76 per cent. of the total humus was immediately soluble in ammonium hydroxide, and in the Kingston soil which stood second in its degree of benefit from liming, but 38.64 per cent. was soluble or much less than in many of the soils where lime proved far less beneficial. The percentage of the total humus which is thus dissolved is not then in any sense a true measure of the lime requirement, though the absolute amounts of humus thus dissolved, have seemed, particularly in our quite heavy soils containing considerable total humus, to correspond with considerable accuracy to the tests with beets.

Though there seems to be no reason to think that there would be any relation between the lime requirement of soils and their total humus on soils of widely divergent character, yet upon soils of analogous mineral origin, it seemed probable that some such relation might exist. The results obtained when plotted in a curve, show, with a few exceptions, the same general trend as those obtained by direct extraction with ammonium hydroxide. In the case of the Jamestown and Harrisville soils the total humus was higher in the former while the amount of humus immediately extracted, was greater in the latter. In the Hamilton soil, the total humus runs too low to accord with the crop test, while the amount of humus immediately soluble in ammonium hydroxide is greater in the case of that soil than in the one at So. Portsmouth, or in agreement with the results secured with beets. In regard to the Kingston and Slocumville soils, the total humus is slightly less in the latter than in the former, but the results come far nearer agreeing with the crop test, than those obtained by immediate extraction of the humus.

In the case of the determination of the lime (calcium oxide) removable from the soil by digestion with hydrochloric acid, the

results are of marked interest, since they show in the most striking manner that the data thus secured with our Rhode Island soils furnished no reliable guide to their lime requirements. As marked illustrations, it will be seen that the Foster Center soil which contained 0.558 per cent. of calcium oxide, or the greatest quantity of any of the soils examined, gave a gain in crop of 291.8 per cent. as compared with a gain from liming of only 21 per cent. in the Warren soil, which yielded only 0.382 per cent. of calcium oxide upon extraction with hydrochloric acid. Again the Slocumville soil showed by extraction with the mineral acid 0.553 per cent. of calcium oxide, or but 0.005 per cent. less than the Foster Center soil, and yet it was benefited by lime more than any other soil tested giving a gain from its use, amounting to 10,080 per cent. The third highest content of calcium oxide as determined by extraction with hydrochloric acid was shown by the Kingston soil, which yielded 0.412 per cent., and yet the only soil which showed a greater benefit from liming was that at Slocumville where the percentage of calcium oxide was even much higher than at Kingston. These examples are sufficient to show that even if by this method of analysis considerable lime, even amounting to more than 0.5 per cent., is shown to be present, it may nevertheless be in such combinations that the soil will almost absolutely refuse to produce certain crops until subjected to liming or other alkaline treatment.

The number of milligrams of nitrogen represented by the ammonia retained by the soil, as determined by the method of titration, accords better with the crop results in the case of the Jamestown and Harrisville soils, than those obtained by immediate extraction with ammonium hydroxide. With the Hamilton soil, the result by the latter method agreed more closely with the crop tests, than those by the former, while in the case of the Kingston and Slocumville soils, the agreement with the crop results was more nearly perfect than those by any other method employed.

Only two tests were made by treatment of the soil with carbonated water. The soil which was the more in need of liming showed by this method a greater quantity of calcium oxide removable by the treatment than the other, or just the reverse of what should have been the case if the method were to

prove of value for the purpose in hand. This fact, together with some experience in the same line in connection with other soils, coupled with the small quantities of calcium oxide removable, gave little reason to hope that the method was applicable for ascertaining the true lime requirements of our acid Rhode Island soils.

The tests by means of the comparison of the color of the ammonium hydroxide extract in the case of the four upper soils in the table, *viz.*, those from Warren, Summit, Jamestown, and Harrisville indicate a gradation in the opposite direction from those with beets. The amount of total humus and the ammonia held by the soil as determined by the method of titration, agree, in the case of these soils, more nearly with the crop results. The results with the Foster Center and South Portsmouth soils, though not showing relative differences in the line of those exhibited by the crop, point, when compared with the first four soils in the series, in the same general way in relation to the soil requirements as the tests with beets. The results with the South Portsmouth and Hamilton soils fail to accord between themselves with the beet test, though the result with the latter soil, when compared with the first four of the series, points in the right general direction. Making a general comparison of the data secured with the Kingston and Slocumville soils with those in connection with the soils standing above them in the table, the tests point to the truth as concerns the needs of the soils. Between themselves the tests would indicate a slightly greater need of lime in the Kingston soil than in the Slocumville soil, or just the opposite of the actual experience.

In closing this consideration of these results, it should be stated that it was recognized at the outstart that unfavorable physical conditions might exert a very disturbing influence, and that in consequence a method which takes into account only chemical defects could not be expected to agree in all cases with the crop results. It was hoped, however, to combine physical analyses of the soil with the chemical, with the idea that possibly by a study of both, one might be helped very materially in arriving at a more correct judgment than by the use of either one singly. The resources at disposal have not as yet made it possible for these determinations to be made. There seemed no reason to



conclude that a physical analysis of the soils only, could come as near revealing their lime requirements as chemical tests, particularly as it had already been abundantly demonstrated<sup>1</sup> that the beneficial action of lime upon our soils is, in a large degree, due to its correcting their prevailing acidity.

#### SUMMARY.

In consequence of the recognition of the acidity of many of the upland soils of Rhode Island and their consequent need of lime, it seemed desirable to find some chemical means for satisfactorily revealing their lime requirements, so as to avoid resorting to the slower and more expensive field experiments.

A number of methods have been tried, as follows:

(1) Moistening the soil with water, then bringing it in contact with blue litmus paper and noting with what rapidity and to what extent it reddens the paper as compared with some soil whose character is already well known. This method is highly effective in the hands of a close observer who has had much experience in testing soils of known character.

(2) Treatment of the soil with water to which a little ammonium hydroxide (ammonia water) has been added and noting whether, after settling, the liquid has assumed a dark brown or black appearance. This test applies only where the acidity is due in a considerable measure to acid organic substances. It may not apply in all sections of the country, as shown by Snyder, in Minnesota, but it has thus far proved a very useful and reliable test with Rhode Island and certain other New England and New York soils containing considerable quantities of humus. Gravimetrically applied this is the method of Müntz.

(3) The method employed by Holleman for determining the lime requirement of stiff clay soils in Holland, based upon the amount of lime (calcium oxide) removable by extracting with carbonated water. This method has given little promise of usefulness in testing our upland acid soils.

(4) The method of Tacke for determining the relative acidity of peat (moor) soils of North Germany based upon the amount of carbon dioxide which the acid ingredients of the soil can expel

<sup>1</sup> Eighth Annual Report, Rhode Island Agricultural Experiment Station, pp. 232-280 (1895); also Ninth Annual Report, pp. 294-318 (1896).

from calcium carbonate at ordinary temperatures in an atmosphere of hydrogen. This method has not seemed to be applicable to our acid upland soils.

(5) The determination of the total humus by a modification of the Grandeau method, which consists in removing the lime and magnesia from their combinations with the humus by treatment with dilute hydrochloric acid, and then dissolving the humus in ammonium hydroxide (ammonia water) and estimating the amount dissolved. In our granitic soils containing considerable quantities of humus, this method gives results standing in somewhat definite relation to the lime requirements.

(6) Determinations of the amount of lime (calcium oxide) which can be dissolved by weak hydrochloric acid by digestion at a high temperature for several hours (official method of the A. O. A. C.). This method furnishes no reliable basis for arriving at the lime requirement of our acid upland soils.

(7) Method by titration, based upon measuring the number of milligrams of nitrogen combined as ammonium salts and held by the soil when it is treated in a given way and for a given time with a very dilute solution of ammonium hydroxide.

The results by this method agree more closely with the crop tests than by any other method tried, though it is closely approximated to, by the gravimetric determination of the humus dissolved from the soil by extraction with ammonium hydroxide without the previous removal of the lime and magnesia.

(8) Method based upon the comparison of the color of the extract made from soils by treating directly with ammonia water, with the color of such an extract prepared from a like quantity of soil of known character. It seems probable that where the acidity is due largely to acid organic substances, this method may give fairly good results. The rapidity with which tests may be made by it is an important practical point in its favor as compared with the method as proposed by Müntz.

(9) Method based upon the amount of carbon dioxide expelled by a given amount of soil from calcium carbonate when the two are heated together at the boiling-point in the presence of water. This method gives promise of much value if the period of heating is made uniform and very brief, and if the carbon dioxide liberated is easily and accurately determined. Routine work

has thus far prevented further attempts to carry out a satisfactory study of this method including the perfection of its details.

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AGRICULTURAL EXPERIMENT STATION.

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### NEW BOOKS.

ANALYSIS OF WHITE PAINTS. A Collection of Notes on the Chemical Analysis of White and Tinted Paints. BY GEORGE H. ELLIS, B.Sc. Evanston, Ills.: The Technical Press. 8vo. pp. 57.

The notes under review were originally published in the *Paint, Oil and Drug Review*, of Chicago, and were prepared and edited by one who has had long practical experience in the technical examination of the products treated. They consist really of a collection of methods for analysis of paints and pigments long used by the author in his daily practice largely devoted to the products of the paint industry, and as the methods have been thoroughly tested and are described in the fullest detail they will be particularly useful to those chemists whose work has given them but limited practice with such products and methods.

With the methods of analysis in each case are presented results obtained by the author in the use of the methods, showing the average composition of the commercial product treated, and thus offers much useful information not easily found elsewhere. The book is commended to those whose duties lead them occasionally in the lines of work here treated and indeed to all needing guidance in the technical examination of pigments and paints.

WM. MCMURTRIE.

THE CHEMISTRY OF SOILS AND FERTILIZERS. BY HARRY SNYDER, B.S., Professor of Agricultural Chemistry, University of Minnesota, and Chemist of the Minnesota Agricultural Experiment Station. Easton, Pa.: The Chemical Publishing Co. 1899. 12 mo. ix + 277 pp. Price \$1.50.

We are told in the preface that this book was intended primarily to be used as a text-book in the author's classes. This fact explains the "experiments" and "review questions" which are given at the end of the book, as well as the condensed manner in which it is written.

It should answer admirably the purpose for which it was intended. The subject-matter is well chosen, well arranged, and clearly and concisely stated.

The style is as nearly popular as is possible with applied chemistry, and the book will be found of value even to agriculturists whose education has not included a course in chemistry.

W. D. BIGELOW.

**A SYSTEM OF INSTRUCTION IN QUALITATIVE CHEMICAL ANALYSIS.** BY ARTHUR H. ELLIOTT, Ph.D. and GEORGE A. FERGUSON, Ph.B. Third edition, revised and enlarged. New York: Published by the Authors. 155 pp. Price, \$1.50.

This manual contains a straightforward, carefully detailed procedure for the systematic qualitative examination of solutions or substances of moderate complexity. The analytical scheme is accompanied by a series of "solution tests" which the student is required to apply to each metal or acid radical and which include the reactions with certain general reagents, and with such special reagents as yield typical products. In connection with these tests a useful list of the important commercial compounds of each metal is given.

Certain of the schemes for the separation of the metals used in former editions have been altered or replaced by others (notably those of the copper and barium groups), and the procedure for the separation and detection of the acid radicals has been enlarged and improved. The book is liberally provided with tabulated statements of the methods of separation, and of the results of the "solution tests." The student can, indeed, hardly go astray within the field covered by the manual, so minute are its directions; yet, under the conditions imposed, the instructor will need to use much effort to encourage independence of thought and action on the part of the student.

The introduction of the "solution tests" is, perhaps, no more a proper subject for criticism in this manual than in many other similar works, but it may fairly be questioned whether so many of these isolated tests do not, by interrupting the study of the systematic plan of analysis, by confusing the beginner and lessening his interest, fail to serve a really useful purpose when the teaching of qualitative analysis is the central aim. To those teachers, however, who favor this method of presentation, the book will appeal strongly as a guide for beginners.

H. P. TALBOT.

**PRACTICAL METHODS FOR DETERMINING MOLECULAR WEIGHTS.** BY HENRY BILTZ, Privatdocent at the University in Greifswald. Translated by HARRY C. JONES and STEPHEN H. KING. Easton, Pa.: The Chemical Publishing Company. 1899. 235 pp. Price, \$2.00.

Previous to the appearance of the German edition of this work there was no satisfactory reference book on the determination of molecular weights, particularly by the vapor-density methods. Windisch's "*Die Bestimmung des Moleculargewichts*" was so voluminous and contained so many processes, with so much descriptive matter that it required an experienced hand to find just what was wanted, and therefore could not be used as a satisfactory laboratory guide. Fuchs's "*Anleitung zur Moleculargewichts Bestimmung*" was entirely satisfactory, but unfortunately was confined to the cryoscopic processes, thus leaving no satisfactory laboratory guide for the vapor-density methods.

This translation places in the hands of English-reading students a masterly summation of the practical methods for determining molecular weights by the vapor-density and the cryoscopic methods, with a careful criticism of the different procedures, and a comparison of the usefulness of one with the other. The author has been strongly under the influence of Victor Meyer, which gives an authoritative value to the Meyer displacement method and its various modifications. The separate methods are described with clearness and with that close attention to essential details which clearly shows the result of much experience. The critical discussion of the results obtained by the various methods is extremely valuable, especially those values obtained from substances which dissociate on heating, and those which suffer electrolytic dissociation in solution. The references to the literature are frequent and form a valuable part of the book.

The book contains chapters on the vapor-density methods of Meyer, Dumas, Gay-Lussac, and Hofmann, with the various modifications; and on the methods for determining molecular weights of substances in solution by the rise in boiling-point and the lowering of the freezing-point. The method of Nernst based on the principle of the lowering of the solubility is treated briefly. The process worked out by Traube and based on a comparison of the values from a determination of the molecular

volume and the theoretical value, is described, but is not recommended.

The translators have done their work satisfactorily. They have added a short chapter on the method and apparatus devised by Jones for the determination of molecular weights by the rise in boiling-point.

HENRY FAY.

THE COST OF LIVING AS MODIFIED BY SANITARY SCIENCE. BY ELLEN H. RICHARDS. 121 pp. New York: John Wiley & Sons. 1899.

This little book is a great disappointment to the student of sanitary science because of the misleading title which it bears. In no single instance has the author given us an idea whether the cost of living has been modified either favorably or unfavorably by sanitary science. She has shown that the cost of living has been increased by various causes which must, however, be classed as economic, social, and industrial.

The principal causes to which she attributes the increased cost of living are: The gross waste on the part of the housewife in reckless and useless expenditure for commodities which are unessential to health and happiness, and the improper utilization and even waste of the commodities purchased; also, the lack of proper interest in her duties, and want of appreciation of the importance of those duties on the part of the housewife. The factors which have brought about the foregoing conditions are mainly industrial, due to the removal of all manufacturing from the home to the factory, changing the occupation of the housewife almost altogether from that of a producer to that of a distributor. It will be seen that none of these causes are traceable to sanitary science.

The subject-matter presented is of marked interest and of the highest importance, and it is unfortunate therefore that it has been presented under a misleading title. Moreover it is to be regretted that the author has not adhered to the title given to the book because there is every reason to believe that the cost of living has been modified by sanitary science and a contribution embodying this information would be most valuable.

D. H. BERGEY.

# THE JOURNAL

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### ON THE ACTION OF CERTAIN ACID REAGENTS ON THE SUBSTITUTED UREAS.

[FIRST PAPER.]

BY F. B. DAINS.

Received March 14, 1900.

IN the course of an investigation on the isourea ethers,<sup>1</sup> the question arose regarding the anilido hydrogen as to its ease of replacement by, and its reactivity toward, acid reagents. Since the amount of experimental evidence concerning the action of acids and acid chlorides on the substituted ureas is relatively small, a study is being made of the behavior of these bodies toward such reagents.

With an easily replaceable hydrogen, a very interesting synthesis would be possible: namely, the direct formation of acyl

thio and oxygen ureas of the general type:

$$\begin{array}{c} \text{RNH} \\ \diagdown \\ \text{CO(S)} \\ \diagup \\ \text{RN} \\ \diagdown \\ \text{COR} \end{array}$$

When, however, acyl chlorides, acid anhydrides, and acids act upon these ureas, while it seems probable in many cases that the

<sup>1</sup> This Journal, 21, 181.

anilido hydrogen is the first point of attack, with the intermediate formation of an acyl derivative, only under especial circumstances have these intermediate bodies been isolated when this method of preparation is used. For instance, the oxygen deriv-

atives  $\begin{array}{c} \text{RNH} \\ \diagdown \\ \text{CO} \\ \diagup \\ \text{RN} \\ \diagdown \\ \text{COR} \end{array}$  have never been prepared directly, but only by

- (1) the addition of acetanilide to phenyl isocyanate,<sup>1</sup>
- (2) the action of acid chlorides on the isourea ethers.<sup>2</sup>

The corresponding sulphur body  $\begin{array}{c} \text{RNH} \\ \diagdown \\ \text{CS} \\ \diagup \\ \text{RN} \\ \diagdown \\ \text{COR} \end{array}$  has, however, been

isolated in the following cases:

(1) Werner<sup>3</sup> heated dibenzyl thiourea and acetic anhydride to the boiling-point of the latter, and obtained acetyl dibenzyl thiourea, besides small quantities of benzyl mustard oil and benzyl acetamide, the usual products of the reaction. Werner thinks that with fatty thioureas such an acyl derivative is usually formed, but he only succeeded in isolating it in the above instance.

(2) Deninger has found that acetyl chloride and thiocarbanilide in pyridine solution give mono acetyl thiocarbanilide.<sup>4</sup>

(3) Recently Hegershoff,<sup>5</sup> by modifying the process used by Werner, and heating the mixture of thiocarbanilide and acetic anhydride only to the temperature of a boiling water bath, succeeded in isolating acetyl thiocarbanilide. A yield of 45 per cent. was obtained, the rest of the thiocarbanilide having formed mustard oil and acetanilide, the products obtained by Werner at the temperature of boiling acetic anhydride.

These acyl ureas are relatively unstable bodies, and readily dissociate above their melting-points into the corresponding cya-

<sup>1</sup> McCreath : *Ber. d. chem. Ges.*, 8, 1181.

<sup>2</sup> Dains : *This Journal*, 21, 182.

<sup>3</sup> *J. Chem. Soc.*, 50, 406.

<sup>4</sup> *Ber. d. chem. Ges.*, 28, 1322.

<sup>5</sup> *Ibid.* (1899), 3649.



nates and anilides, thus giving opportunity for secondary reactions.

While it seems extremely probable, and in a number of cases is definitely proved, that the acid chlorides and anhydrides react with the ureas with the formation of such intermediate acyl ureas, yet under the conditions of the experimental work in this paper, the temperature required to produce reaction was so high that such acyl ureas were never isolated, but only their decomposition products. This fact has given rise to some interesting results.

The work in this paper has been confined to a study of the action of acids and acid chlorides on such ureas as carbanilide and thiocarbanilide, the only exception being some experiments on the action of acetic anhydride and the above reagents on the oxygen and sulphur isourea ethers. The interaction between these reagents and the monosubstituted and acyl ureas will be discussed in a later paper.

#### EXPERIMENTAL.

*Organic Acids and Carbanilide.*—Werner<sup>1</sup> has shown that pure acetic acid decomposes diphenyl urea at 160°–170°, giving acetanilide, carbon dioxide, and water.

*Organic Acids and Thioureas.*—Cain and Cohen, while investigating the “action of acetic acid on phenyl thiocarbamide,” heated absolute acetic acid and thiocarbanilide at 130°–140° for three to four hours. They simply state that diphenyl urea was one of the products.<sup>2</sup> This is wholly in accord with the general action of anhydrous acids at temperatures above 130°. At a lower temperature, somewhat different results are obtained. Thus 9 grams of thiocarbanilide and 20 cc. of pure acetic acid were heated in a water-bath for thirty hours. The residual solid, when filtered off and examined, proved to be thiocarbanilide, and not diphenyl urea. On distilling the acid filtrate with steam, phenyl mustard oil came over, while the distilling flask was found to contain acetanilide and a base that melted at 145°,—its picrate melted at 180°, and was, therefore, triphenyl guanidine. The picrate of pure triphenyl guanidine was found by

<sup>1</sup> *J. Chem. Soc.*, 59, 550.

<sup>2</sup> Cain and Cohen : *J. Chem. Soc.*, 59, 328.

experiment to melt at  $180^{\circ}$ , and not at  $178^{\circ}$ , as given in the literature.

Under these conditions, then, the reaction follows out the lines of the decomposition of the thiocarbanilides with aqueous hydrochloric acid, the difference centering in the fact that the products of the reaction tend to form anilides with the organic acid present,—a tendency more apparent when higher temperatures are used. In this case there is first dissociation into phenyl mustard oil and aniline; and as secondary reactions, the formation of acetanilide from the aniline and the glacial acetic acid, and also, though more slowly, from the acid and the mustard oil. This interpretation is confirmed by the fact that, while at the above temperature no carbanilide is formed when absolute acid is used, with aqueous acid diphenyl urea is produced (as shown by experiment). This, as the investigation of Werner shows, is due to the action of the aqueous acid upon the phenyl thiocarbamide. It was found by direct experiment that the final products of 75 per cent. acetic acid, and thiocarbanilide at water-bath temperature are acetanilide and diphenyl urea, although the odor shows that mustard oil is an intermediate product.

*Butyric Acid and Thiocarbanilide.*—2.3 grams of thiocarbanilide and 2 grams of butyric acid were heated at  $140^{\circ}$ – $160^{\circ}$  for two hours. Reaction set in with the evolution of carbon dioxide and hydrogen sulphide. From the residue, by crystallization from alcohol, there was isolated butyric anilide and diphenyl urea. Carbon oxysulphide was probably evolved, but no effort was made to detect it in the presence of hydrogen sulphide and carbon dioxide. In all of these experiments, it may be said, traces of the free amine could be detected.

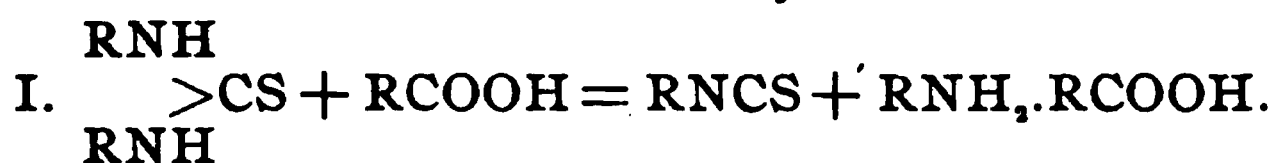
*Benzoic Acid and Thiourea.*—Molecular quantities of benzoic acid and diphenyl thiourea, at  $160^{\circ}$ – $180^{\circ}$ , evolve hydrogen sulphide, carbon dioxide, and water. As the formation of gas ceases, the melt becomes semisolid, and on examination is found to consist of a little benzoic acid which was extracted with dilute alkali, benzanilide, and a small amount of diphenyl urea.

Diparatolyl thiourea and benzoic acid, under like conditions, gave as gaseous products carbon dioxide and hydrogen sulphide, and a residue of *p*-benztoluid *p*-carbtoluid, and a little benzoic acid.

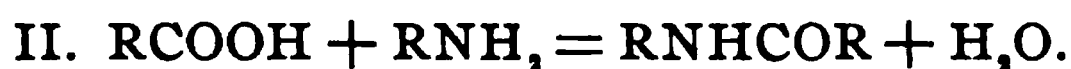
*Salicylic Acid and Diphenyl Thiourea.*—A mixture of these bodies in molecular proportions, when heated, liquefied at  $140^{\circ}$ , and at  $150^{\circ}$  slowly gave carbon dioxide and hydrogen sulphide. Caustic alkali separated the melt into two portions: one soluble in alkali, the other insoluble. This latter proved to be diphenyl urea. The portion soluble in the caustic soda consisted of salicylic anilide (m. p.  $133.5^{\circ}$ ) and a little salicylic acid. Besides these products traces of aniline and phenol were formed,—the latter doubtless due to a slight decomposition of the salicylic acid.

The experiments presented show that the reaction between the thioureas and organic acids of the type  $\text{RCOOH}$ , proceeds along fairly definite lines. The products to be accounted for are carbon dioxide, hydrogen sulphide, water, the anilide, mustard oil and carbanilide.

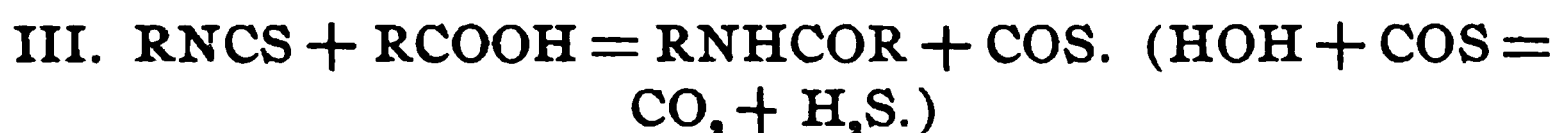
The main reaction is the one already indicated:



At the temperature of the reaction the amine and the acid unite.



At the same time the mustard oil is attacked.



Only the carbanilide remains to be accounted for. This body, it will be remembered, is produced only when high temperatures are used in the reaction between thiocarbanilide and anhydrous acids. At the water-bath temperature none was formed. Werner, who has studied the reaction between acetic acid and phenyl mustard oil, says that the decomposition occurs according to the following equation:<sup>1</sup>



In view of this it might be said that the carbanilide is due to the water formed in the reaction and the mustard oil set free at the same time. But such a conclusion must be erroneous for the following reasons:

*a.* At water-bath temperature none is formed;

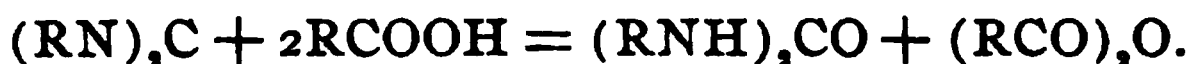
<sup>1</sup> *J. Chem. Soc.*, 59, 545.

*b.* Much, if not all, of the water escapes at the temperature of the reaction;

*c.* More carbanilide is often produced than the above equation accounts for.

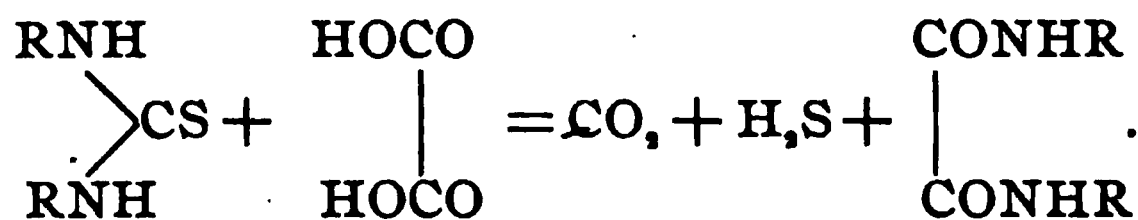
A very probable hypothesis is the following: at the high temperature employed, there is more or less dissociation of the thiocarbanilide into carbodiimide and hydrogen sulphide.

The carbodiimide thereupon reacts with the organic acid as follows:<sup>1</sup>



*Dibasic Acids and the Thioureas.*—Diphenyl thiourea and oxalic acid were heated at 160°–170°. The mixture melted readily, decomposed with the evolution of gas, and then partially solidified.

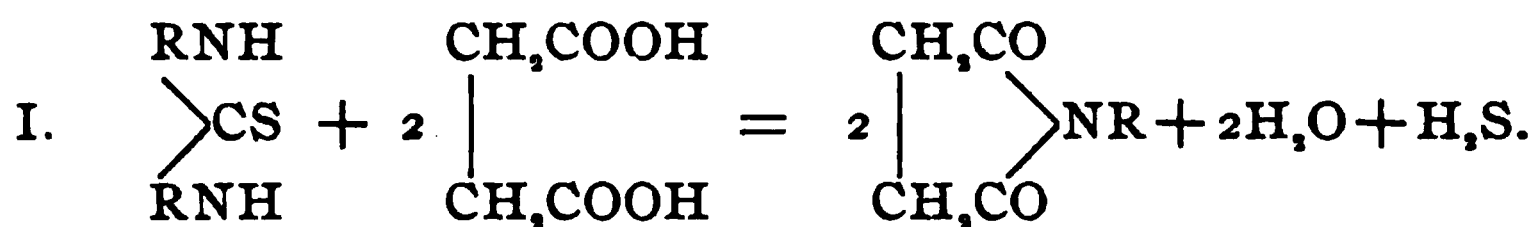
The gaseous products consisted mainly of carbon dioxide and hydrogen sulphide. From the solid residue, hot alcohol extracted traces of phenyl mustard oil and a little unchanged thiourea. The insoluble portion proved to be oxanilide (m. p. 240). The main reaction, then, is as follows:



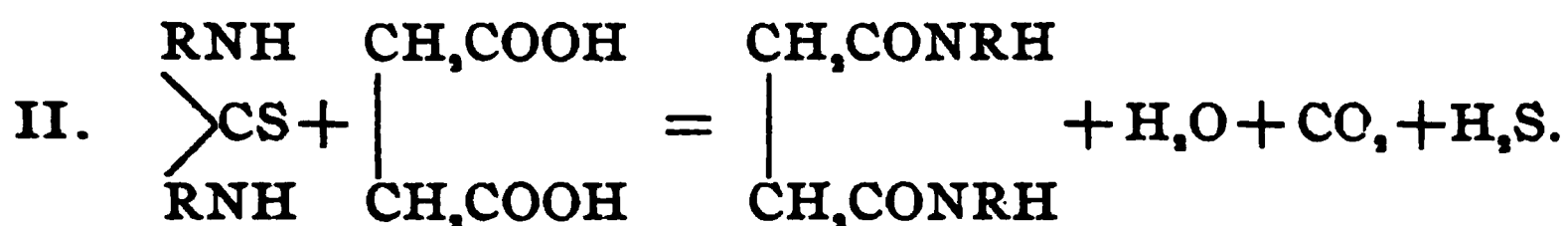
Traces of aniline could also be detected, probably in the form of aniline oxalate. No oxanilide was discovered.

Thiocarbanilide (11 grams) and succinic acid (5 grams) require a temperature of 170° before reaction sets in. At this point, however, much carbon dioxide, hydrogen sulphide, and water are evolved. The other products consisted of small amounts of aniline and mustard oil, while the residual solid could be separated by fractional crystallization into succinanil and succinanilide.

The main results can be expressed as follows:—



<sup>1</sup> Dains: This Journal, 21, 157.



These reactions are almost identical with those that occur when the anhydride is used instead of the acid. For instance, Dunlap<sup>1</sup> has found that succinic anhydride and thiocarbanilide give succinanil, succinanilide, carbonyl sulphide, and aniline. My own experiments confirm these results and show that with the elevation of temperature, there is increase in the amount of succinanilide formed. Thus, equal molecules of di-*p*-tolyl thiourea and succinic anhydride, when heated at 160°–180°, give as gaseous products carbon dioxide, hydrogen sulphide, water, and COS. The residue consisted of *p*-tolylsuccinimid and *p*-succin-toluid.

It is possible that formation of succinic anhydride precedes the interaction with the thiocarbanilide, as seems to be the case with phthalic acid.

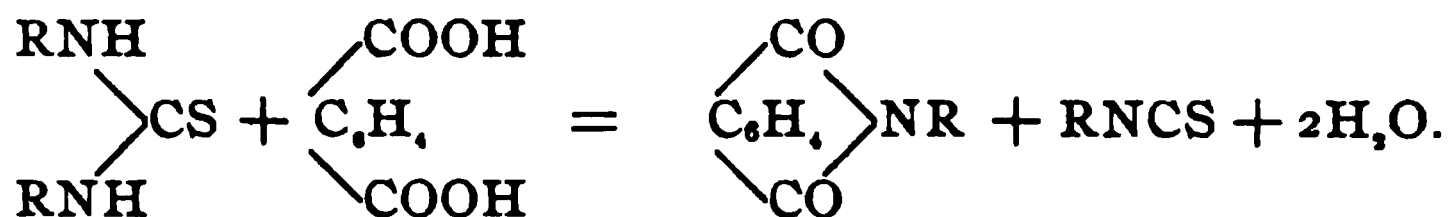
Thiocarbanilide and phthalic acid (equal molecules) reacted at 170°, with the evolution of hydrogen sulphide and carbon dioxide.

The residue was washed with cold alcohol: this removed, as was found, phenyl mustard oil, a little aniline, and a solid melting at 125°–130° which proved to be phthalic anhydride. The main product, which was insoluble in the cold alcohol, proved to be phthalanil (m. p. 205°). The reaction proceeds as if the anhydride had been used instead of the acid. The results again are in accordance with the experiments of Dunlap<sup>1</sup> who found that thiocarbanilide and phthalic anhydride react at 170° with the formation of phthalanil and mustard oil.

Before this paper of Dunlap's was seen, experiment showed that *p*-tolyl thiourea and phthalic anhydride react easily and smoothly at 160° yielding COS, traces of water and hydrogen sulphide, and practically quantitative amounts of *p*-tolyl mustard oil and *p*-tolyl phthalanil. An excess of the acid or acid anhydride increases the yield of phthalanil and decreases that of the mustard oil, since it was found by experiment that equal mole-

<sup>1</sup> *Am Chem. J.*, 18, 332.

cules of phthalic anhydride and mustard oil at 160° slowly give COS and phthalanil. On the contrary phenyl mustard oil and succinic anhydride do not react at 180°, but when boiled together tar is produced and an odor of phenyl isocyanate developed.

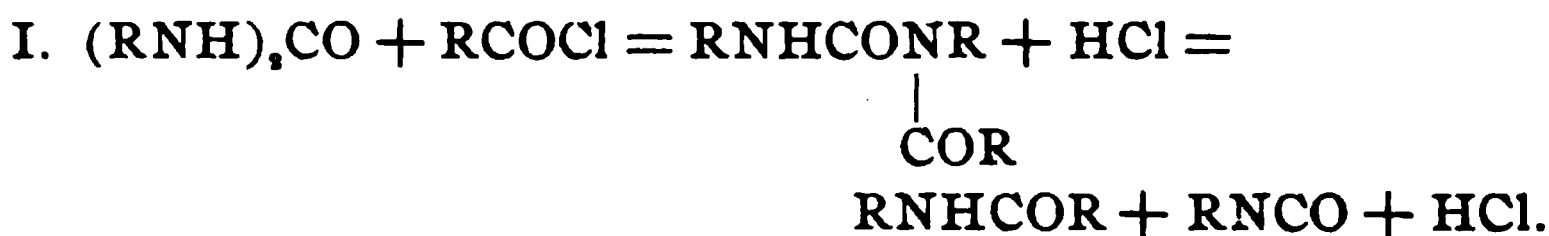


*Acid Chlorides and Ureas.*—When acid reagents like the acid anhydrides and the acid chlorides act upon the disubstituted ureas, the anilido hydrogen seems to be the main point of attack, although the actual mechanism of the reaction, whether it be one of addition or direct replacement of the hydrogen, cannot as yet be settled experimentally. The evidence points, however, to the intermediate formation in some way of an acyl derivative.

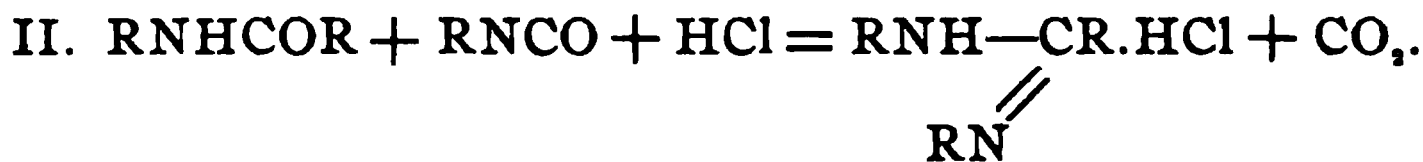
With the oxygen ureas such a compound,  $\begin{array}{c} \text{RNH} \\ \diagup \\ \text{CO} \\ \diagdown \\ \text{RN} \end{array} \text{COR}$ , can

never be obtained by the direct action of the acid chloride since the acyl body decomposes at a temperature below that at which the reaction is carried out.

The equations evolved in the interaction of an acid chloride and carbanilide can be represented as follows:



Under the conditions of the experiment, the acyldialphyl urea breaks down into an anilide and isocyanate, which in turn react, giving carbon dioxide and an amidine derivative.



Diphenyl urea was heated with a slight excess over 1 molecule of acetyl chloride in a sealed tube for three hours at 150°. The tube opened with pressure due to carbon dioxide and a little

hydrochloric acid. After the addition of water the reaction-product was shaken out with ether. This removed acetanilide.

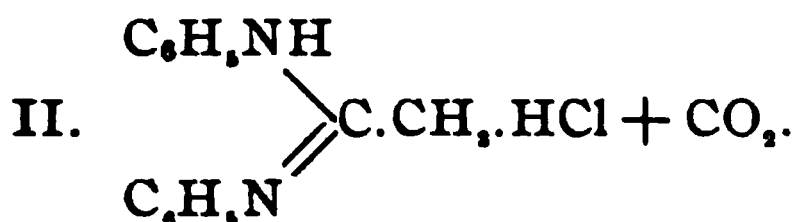
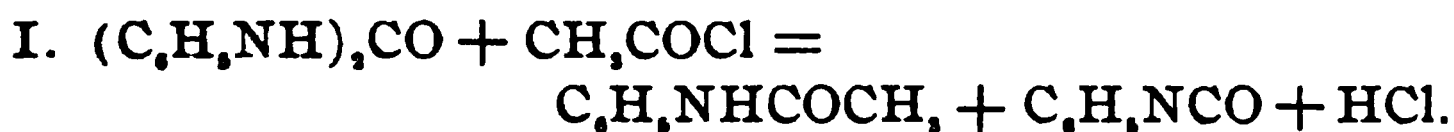
On treating the water solution with an alkali, a base was precipitated which, on examination, was found to be acetdiphenylamidine, m. p.  $131^{\circ}$ – $132^{\circ}$  ( $\alpha$ -phenylimido- $\alpha$ -phenylamidoethane). This base can be purified by recrystallization from alcohol or by dissolving in benzene, passing in hydrogen chloride, and then extracting the pure hydrochloride with water. This removes gummy impurities that are apt to remain persistently with the base. It was further identified by its platinum salt, which melted at  $210^{\circ}$ .

Analysis of two separate preparations :

1. 0.1810 gram substance gave 0.0430 gram platinum.
2. 0.1400 gram substance gave 0.0326 gram platinum.

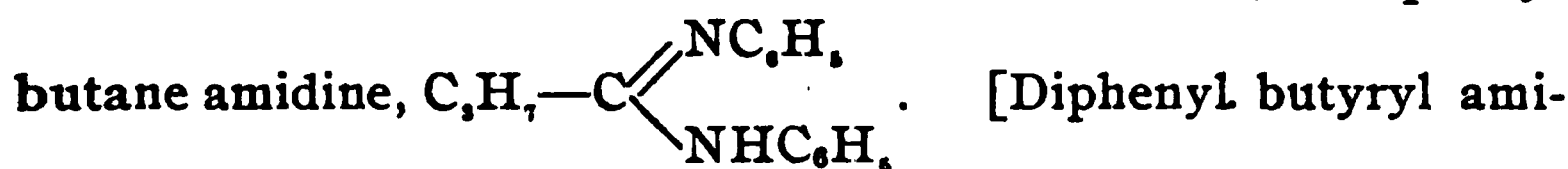
	Calculated for (C <sub>14</sub> H <sub>14</sub> N <sub>2</sub> ) <sub>2</sub> H <sub>2</sub> Pt.Cl <sub>6</sub> .	Found.	
		1.	2.
Platinum .....	23.47	23.75	23.30

The picrate of this base melts at  $165^{\circ}$ .



Nine grams carbanilide and 5 cc. butyryl chloride were heated at  $150^{\circ}$ – $170^{\circ}$  for four hours. The tube opened with much pressure due to carbon dioxide and hydrogen chloride. The contents, which formed an oily mass filled with bubbles of gas, were dissolved in alcohol and the alcohol evaporated to remove excess of the acid chloride. The ether extract gave 0.5 gram of butyric anilide, which crystallized from ligroin in square plates.

The water solution was found to contain a base,  $\alpha$ -diphenyl



This crystallizes from alcohol, in which it is very soluble, in fine star clumps of needles, which melt at  $105^{\circ}$ .

Analysis resulted as follows :

0.600 gram substance (Kjeldahl) required 4.9 cc. normal acid.

	Calculated for $C_{10}H_{10}N_2$ .	Found.
Nitrogen.....	11.78	11.46

When a solution of the amidine hydrochloride and chlorplatinic acid is allowed to evaporate slowly, a red platinum salt is produced.

Analysis gave the following :

0.3780 gram salt gave 0.0832 gram platinum.

	Calculated for $C_{22}H_{22}N_2PtCl_6$ .	Found.
Platinum .....	21.98	22.01

Molecular proportions of carbanilide and benzoyl chloride were heated at  $160^{\circ}$ – $170^{\circ}$  for four hours. As before, carbon dioxide was formed. From the solid contents of the tube, benzene extracted benzanilide, m. p.  $161^{\circ}$ . The residue insoluble in benzene dissolved readily in water and proved to be the hydrochloride of a base, diphenyl benzenyl amidine, formed by the action of the phenyl isocyanate on the benzanilide.

Thus Kuhn<sup>1</sup> has shown that phenyl isocyanate and benzanilide react at  $180^{\circ}$ – $200^{\circ}$  to form the above amidine and carbon dioxide. The base that melted at  $145^{\circ}$  was further identified by its platinum salt. This melted at  $212^{\circ}$  and gave the following figures on analysis :

0.1892 gram substance gave 0.0382 gram platinum.

	Calculated for $C_{26}H_{26}N_4PtCl_6$ .	Found.
Platinum.....	20.39	20.19

When molecular proportions of benzoyl chloride and carbanilide are heated in an open flask at  $160^{\circ}$ – $200^{\circ}$ , carbon dioxide and hydrochloric acid are given off and the intermediate formation of phenyl isocyanate is very apparent from the odor. Diphenyl benzenyl amidine was isolated as before and was identified by its own melting-point and that of its picrate (m. p.  $216^{\circ}$ ).

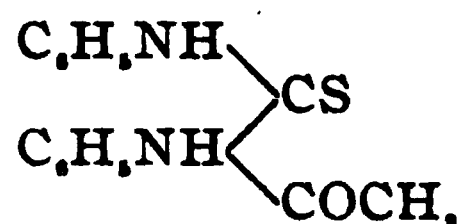
*Acyl Chlorides and Dialphyl Thioureas.*—Reagents of this class act more readily on the thioureas than on the corresponding oxygen derivatives. The products of the reaction are largely dependent upon the following conditions: the presence of a solvent such as pyridine, the temperature, and the fact that the mustard oils

<sup>1</sup> *Ber. d. chem. Ges.*, 18, 1476.



are less reactive than the corresponding isocyanates, and so do not tend to react with the anilide formed.

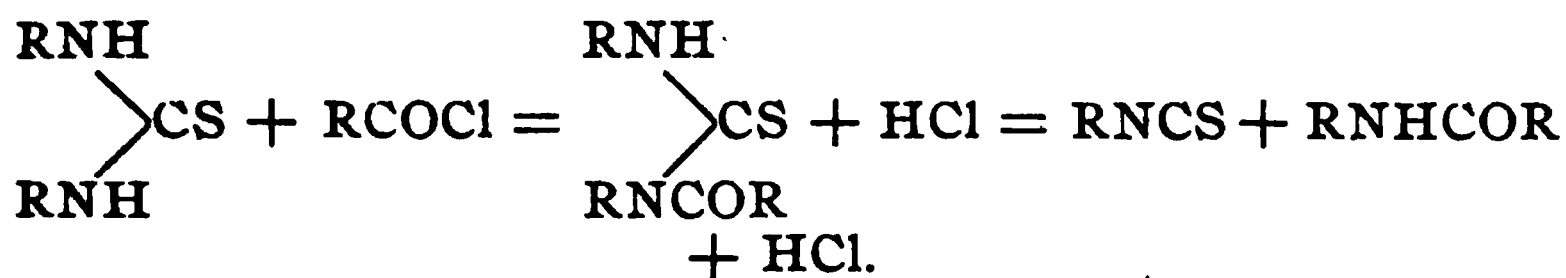
Deninger<sup>1</sup> has shown that by dissolving thiocarbanilide in pyridine, acyl chlorides attack the anilido hydrogen with great ease at ordinary temperatures, forming a stable substitution product. For instance, acetyl chloride and thiocarbanilide, under these conditions, give acetyl thiocarbanilide.



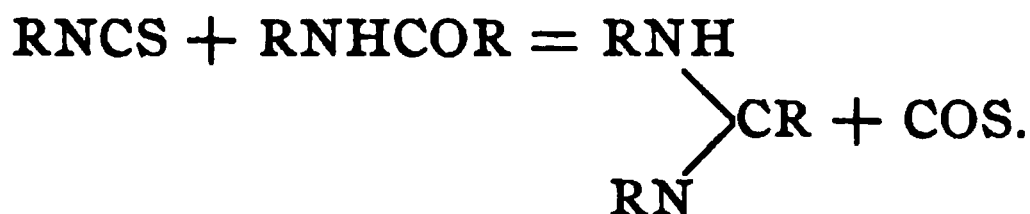
With benzoyl chloride and diphenyl thiourea, a dibenzoyl derivative was obtained. Like the oxygen bodies of similar constitution, these acyl thiocarbanilides are easily decomposed. Thus, acetyl thiocarbanilide, when heated above its melting-point or when boiled with water, gives phenyl mustard oil and acetanilide, which two components show no tendency to unite again even when heated. On the other hand, phenyl isocyanate and acetanilide heated in a sealed tube to 150° unite to form acetyl diphenyl urea.<sup>2</sup>

In the absence of pyridine, which combines with the hydrochloric acid set free, my experiments show that heat is required to effect complete reaction between the acyl chloride and the thioureas, and that under these conditions no intermediate product corresponding to the acyl thiocarbanilide can be isolated.

The general reaction between an acyl chloride and a dialkyl thiourea can be expressed as follows :



Mustard oil and an acyl anilide are the main products, while occasionally small quantities of an amidine base are formed.



<sup>1</sup> *Ber. d. chem. Ges.*, 28, 1332.

<sup>2</sup> McCreath : *Ibid.*, 8, 1181.

*Acetyl Chloride and Thiocarbanilide.*—Diphenyl thiourea was treated with a slight excess over 1 molecule of acetyl chloride, and, as no reaction occurred at ordinary temperatures, the mixture was warmed to 50° on the water-bath, until the evolution of hydrochloric acid ceased. The oily product, which became semisolid on cooling, was distilled with steam. Phenyl mustard oil came over. This was identified by its properties, and the formation of monophenyl thiourea. On concentrating the water solution of the residue not volatile with steam, acetanilide (m. p. 114°) was obtained. The filtrate from this, when neutralized with alkali, gave small quantities of a base which proved to be acetdiphenyl amidine, a product formed in much larger quantities in the reaction between acetyl chloride and carbanilide, and identical with the body thus obtained.

Butyryl chloride and diphenyl thiourea react with ease, giving much hydrochloric acid, and an oily product from which can be isolated phenyl mustard oil and butyric anilide. Small amounts of an impure base are also formed.

When molecular quantities of benzoyl chloride and thiocarbanilide are heated to 150°, reaction ensues with the evolution of hydrogen chloride, a little carbon dioxide, and a gas that blackens lead acetate paper. On distilling the product with steam, or by separating with cold alcohol, there can be isolated almost quantitatively phenyl mustard oil and benzanilide. Traces of the base diphenylbenzenyl amidine are also formed.

Di-*m*-xylyl thiourea and benzoyl chloride, under like conditions, react at 120°. The products were the benzoyl derivative of metaxylidine ( $\text{CH}_2\text{CH}_2\text{NH}_{1,3,4}$  (m. p. 192°), and xylyl mustard oil, which, with alcoholic ammonia, gave the monothiourea (m. p. 175°). Traces of an impure base were also formed.

Greater elevation of temperature does not favor this reaction between the acid chlorides and the thioureas. For instance, molecular quantities of benzoyl chloride and di-*o*-tolyl thiourea were heated in a sealed tube at 180°–200°. The tube opened with slight pressure, and the issuing gas burned with a pale blue flame. The contents of the tube consisted of *o*-tolyl mustard oil, *o*-benztoluide, much tar, and a small amount of an impure base.

Allylphenyl thiourea was warmed on the water-bath with a slight excess of acetyl chloride. The reaction-product formed a

thick oil, with the evolution of a little hydrogen chloride. On distilling this oil with steam, a few drops only of phenyl mustard oil were obtained, and the residue in the distilling flask, with the exception of a little tar, was completely soluble in water. From this, alkali threw down a base which, without further purification, melted at  $115^{\circ}$  and gave a picrate (m. p.  $153^{\circ}$ ). It was, therefore, *N*-phenylpropylene pseudo thiourea. (2-Phenylamido-5-methyl-4,5-dihydrothiazol.) This was further established by the analysis of the platinum salt.

0.6003 gram substance gave 0.1477 gram platinum.

	Calculated for (C <sub>10</sub> H <sub>13</sub> N <sub>2</sub> S) <sub>2</sub> H <sub>2</sub> PtCl <sub>6</sub> .	Found.
Platinum .....	24.53	24.60

The acyl chloride evidently causes a practically quantitative rearrangement. Boiling with hydrochloric acid brings about the same change.<sup>1</sup>

*The Action of Acid Reagents on Isourea Ethers.*—A study begun in a former paper on the action of acids, acid chlorides, and acid anhydrides on the isourea ethers is here continued and extended to the corresponding sulphur ethers.

Organic acids act with great ease upon the isourea ethers. Thus ethylisodi-*o*-tolyl urea and glacial acetic acid give ethyl acetate and carbanilide, as has been shown in a former paper.<sup>2</sup>

Towards acids and acid reagents the thio ethers show remarkable stability. Ethylisothiocarbanilide can be boiled with glacial acetic acid without effect, the original base being recovered unchanged. When heated at  $180^{\circ}$  with acetic acid the tube opens with pressure; the issuing gases burn and form a white precipitate with a silver nitrate solution. The solid residue consists of pure acetanilide. The odor of mercaptan is apparent.

*Acid of Acetic Anhydride upon the Oxygen Urea Ethers.*—Ten grams of amylisodi-*o*-tolylurea and 3.5 grams of acetic anhydride were mixed. Since no apparent reaction took place after standing at ordinary temperatures, the solution was heated in an oil-bath at  $150^{\circ}$ – $160^{\circ}$  for one and one-half hours. The product, which remained oily after twelve hours' standing, was distilled at 12 mm. pressure; there was isolated amyl acetate, a

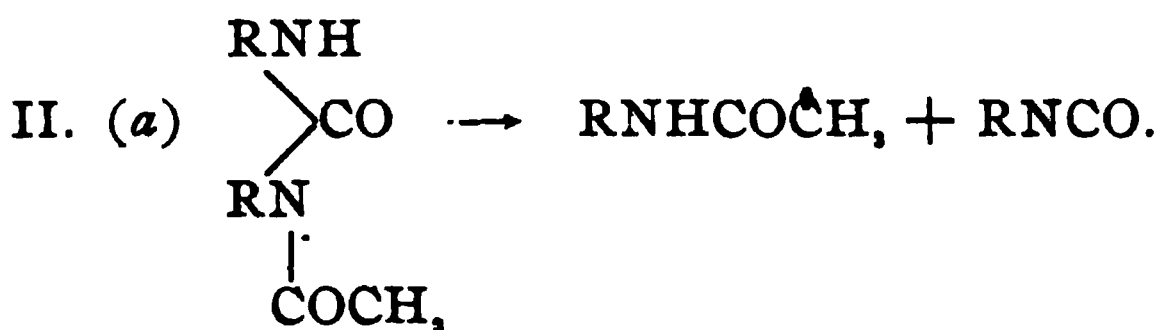
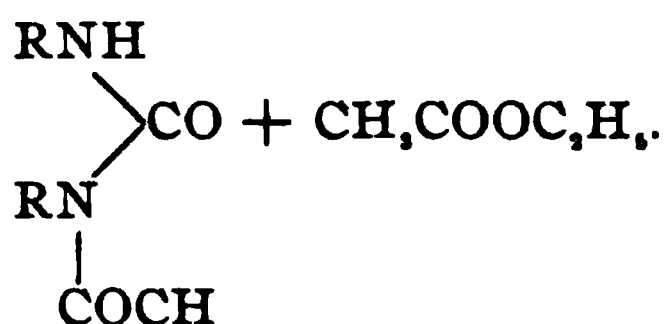
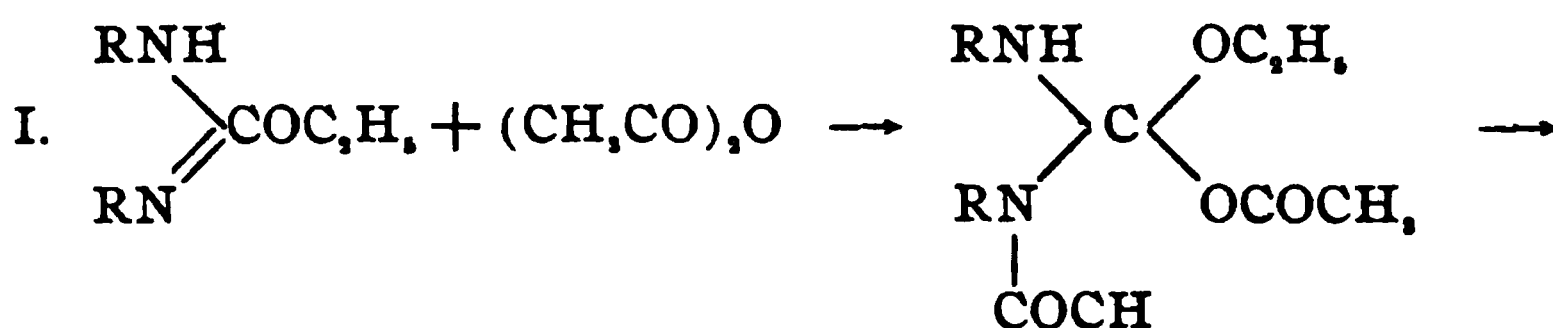
<sup>1</sup> Prager: *Ber. d. chem. Ges.*, 22, 2991.

<sup>2</sup> This Journal, 21, 170.

little unchanged acetic anhydride, *o*-acettoluide, and a trace of *o*-ditolylurea. The latter may be due to traces of moisture or of acetic acid in the anhydride.

Equal molecules of ethyl isocarbanilide and of acetic anhydride were heated in a test-tube fitted with an air-condenser and a calcium chloride tube for eight hours at 160°–170°. Ethyl acetate was detected by its odor. The oily product was treated with alcohol to get rid of the excess of the acetic anhydride and then recrystallized from water. Acetanilide was isolated. This same reaction was found to take place with equal ease at 130°–140°. At this latter temperature methylisocarbtoluide and acetic anhydride give methyl acetate and *o*-acettoluide. The yield of acetanilide or of *o*-acettoluide seems to be quantitative.

As in all reactions with acidic reagents there is doubtless first addition to the double bond with the formation of an unstable addition-product.



At the temperature of the experiments, 130°–140°, not only is this intermediate addition-product broken down, but the acetyl diphenyl urea formed is dissociated into phenyl cyanate and acetanilide: and the phenyl cyanate in turn reacts with the excess of acetic anhydride to form diacetanilide. That the diacetani-

lide was not isolated is not surprising, since it is very easily saponified.<sup>1</sup>

The experimental evidence for equation II is as follows :

(a) Acetyl diphenyl urea, when heated a little above its melting-point, dissociates, giving phenyl isocyanate and acetanilide.

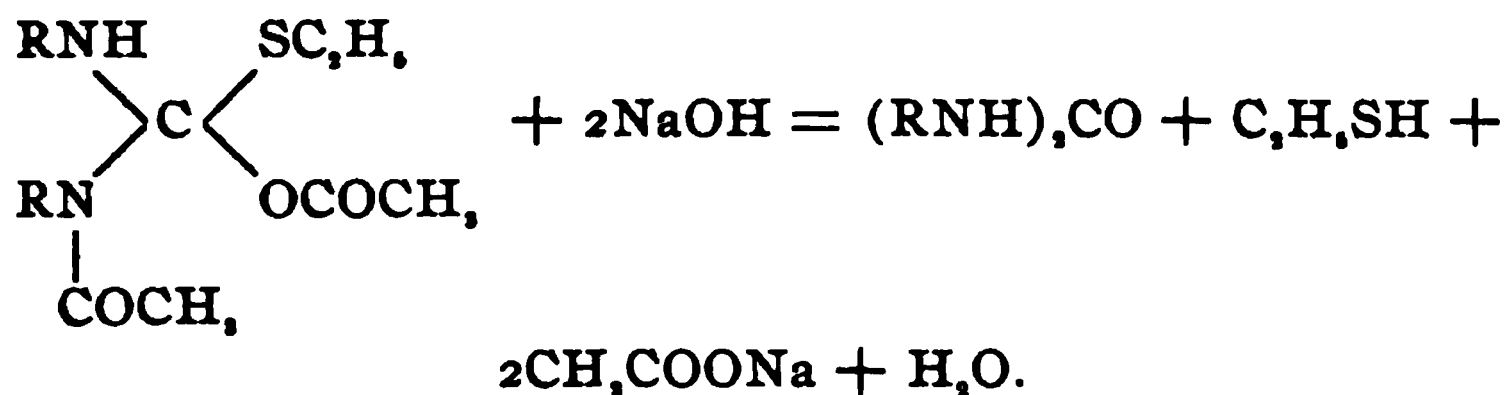
(b) Acetyl diphenyl urea, when heated with acetic anhydride at 130° for two hours, and the resulting product recrystallized from water, gives a quantitative yield of acetanilide.<sup>2</sup>

(c) Phenyl isocyanate and acetic anhydride give acetanilide.

In the oxygen ethers, the existence of an intermediate product due to the addition of the acid anhydride to the double bonding of the ether was assumed. With the thioethers the existence of such an addition-product was definitely proved.

Ethyl isodiphenyl thiourea and acetic anhydride can be heated to the boiling-point of the latter without seeming change, or the formation of ethyl acetate; and on careful treatment with alkali, the original base can be regenerated.

If, however, the excess of anhydride be decomposed with alcohol, the resulting oil is no longer soluble in dilute mineral acids. Alcoholic potash yields mercaptan and carbanilide, the decomposition taking place with great ease. An effort was made to purify this oil by dissolving in ether and washing with dilute sodium carbonate and water, and drying. The evaporation of the ether left a yellow oil insoluble in water and dilute alkalies. Experiment showed that alcoholic potash gave, on warming with this, mercaptan and diphenyl urea. Hence, if the body is the expected addition-product, it must decompose as follows :



The oil was analyzed by dissolving it in alcohol, adding a definite quantity of standard sodium hydroxide, boiling with a reflux

<sup>1</sup> Gumpert (*J. prakt. Chem.*, 31, 121), who tried the action of phenyl isocyanate and acetic anhydride, obtained only acetanilide, a result probably due to moisture.

<sup>2</sup> Experiments have shown that diphenyl urea and boiling acetic anhydride give acetanilide and carbon dioxide.

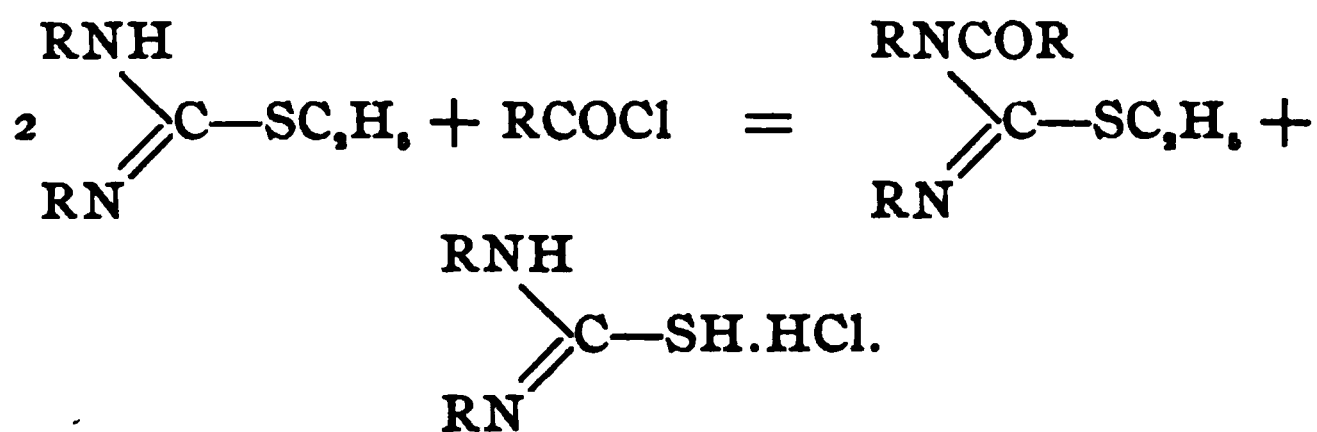
condenser until decomposition was effected, and then titrating the excess of alkali, using phenol phthalein as an indicator. The amount of acetic anhydride could thus be determined, since 1 cc. normal alkali is equal to 0.05103 gram acetic anhydride.

1. 1.7065 grams substance required 9.3 cc. alkali.
2. 1.7965 grams substance required 9.76 cc. alkali.

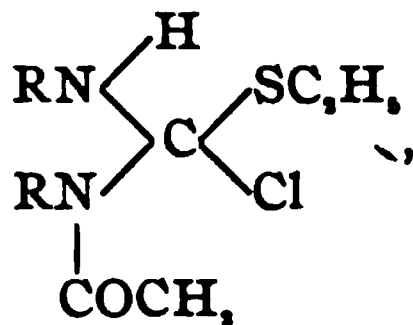
	Calculated for $C_{19}H_{22}N_2O_2S$ .	Found.	
		1.	2.
$(CH_3CO)_2O$ .....	28.48	27.81	27.72

The difficulty of purifying such a compound, and the ease with which it breaks down, account for the low results. At high temperatures complete reaction follows between the acetic anhydride and the ethyl isothiocarbanilide. Thus, after heating at  $190^\circ$ , the tube opened with pressure due to inflammable gases, while mercaptan and ethyl acetate were recognized by the odor. The solid residue in the tube was pure acetanilide.

*Action of Acetyl Chloride upon Ethyl Isothiodiphenyl Urea.*—Experiments in a previous paper<sup>1</sup> have shown that with the oxygen urea ethers, acid chlorides react, giving, by addition and subsequent decomposition, ethyl chloride and acyl diphenyl urea. With the sulphur derivatives the reaction proceeds in an entirely different manner, due doubtless to the greater stability of the thio ethers toward acid reagents, and to the more negative character of the molecule. The general reaction between the thio ethers and acid chlorides is as follows :



Either the anilido hydrogen is replaced directly by the acyl group, or there is first, addition to the double bond,



<sup>1</sup> This Journal, 21, 181.

and then loss of hydrogen chloride, which unites with a second molecule of the urea ether to form the hydrochloride.<sup>1</sup>

Two molecules of the thioether were dissolved in chloroform and treated with 1 molecule of acetyl chloride. After standing for twenty-four hours, the solution was washed with water, the excess of chloroform evaporated, and the residual oil taken up with ether; this was washed again with a solution of sodium bicarbonate to remove all traces of free acid. After drying, the evaporation of the solvent left a thick oil, which could not be crystallized, and was no longer soluble in dilute acid. This was analyzed, as in the previous case, by boiling in an alcoholic solution with a standard caustic alkali, the products being sodium acetate, mercaptan, and carbanilide.

1.3554 grams substance required 4.545 cc. normal NaOH. This is equivalent to 0.1954 gram  $\text{CH}_3\text{CO}$ .

	Calculated for	
	$\text{C}_6\text{H}_5\text{N} \begin{array}{l} \diagup \text{COCH}_3 \\ \diagdown \text{CSC}_6\text{H}_5 \end{array}$	Found.
$\text{CH}_3\text{CO}$	14.42	14.41

This body, monoacetylethylisodiphenyl thiourea, is interesting as being the first acyl derivative of the isourea ethers that has been isolated. The action of this substance toward glacial acetic acid has also a direct bearing upon the mechanism of the acetic anhydride reaction described on page 195.

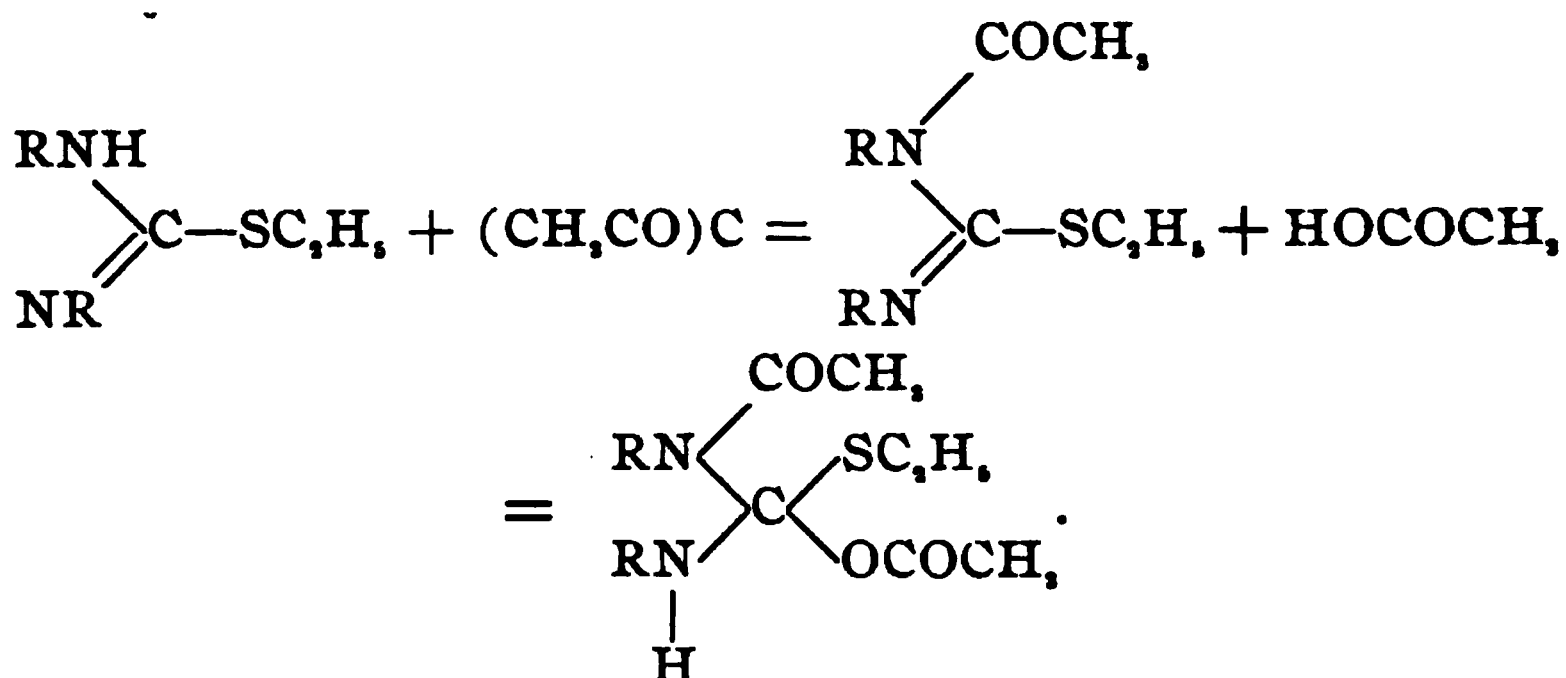
Thus, when acetyl ethyl isodiphenyl thiourea was heated to the boiling-point with an excess of glacial acetic acid and allowed to stand for twenty-four hours, the product then being poured into water and purified as in the preceding cases, the original oil was recovered, and not an acetic acid addition-product identical with the product from acetic anhydride.

0.7420 gram oil required 4.9 cc. half-normal NaOH.

	Calculated for	
	$\text{C}_{17}\text{H}_{18}\text{ON}_2\text{S}$	Found.
$\text{CH}_3\text{CO}$ .....	14.42	14.33

This points to the conclusion that the acetic anhydride acts by direct addition to the double bond, and not by first replacing the anilido hydrogen with an acetyl group and then adding acetic acid, as follows :

<sup>1</sup> *Am. Chem. J.*, 19, 136.



*Action of Benzoyl Chloride.*—Ten grams of ethyl isodiphenyl thiourea and 3 grams of benzoyl chloride were dissolved in benzene and allowed to stand for a week. The crystals that separated weighed 5.7 grams and consisted of the pure hydrochloride of the ethyl ether (m. p. 178°). After distilling off the benzene, an oil was left, insoluble in ammonia or dilute hydrochloric acid, the benzoyl ethyl thiodiphenyl urea. It was not obtained pure enough for analysis. An effort was made to distil the oil but decomposition ensued, with the formation of much tar, some phenyl isocyanate, and carbodiphenyl imide. Another portion heated in a sealed tube with hydrochloric acid, at 140°, gave ethyl chloride, carbon dioxide, mercaptan, aniline, and benzoic acid, so that while the body was not analyzed, its identity is fairly well established.

NORTHWESTERN UNIVERSITY CHEMICAL LABORATORIES,  
2421 DEARBORN ST., CHICAGO,  
March, 1900.

## THE TECHNICAL ESTIMATION OF ZINC.

BY ALBERT H. LOW.

Received February 26, 1900.

IN a report read June 11, 1892, before the Colorado Scientific Society, the method devised by the writer for the technical estimation of zinc in ores, etc., was approved as the best that had come to the attention of the committee. Although it had its weak points, some of which were recognized at the time, it was nevertheless well adapted for rapid and accurate work on the majority of Colorado ores and, in fact, no better method has since been offered.



Applications for a description of the method are very frequent, and in view of the fact that daily use in the laboratory for several years has naturally resulted in some changes from the original plan, it may not be out of place to again publish the scheme in its latest form. It is, of course, apparent that the method as given is not of universal application. Sometimes a fusion may be necessary to effect complete decomposition, or perhaps a preliminary treatment with hydrochloric acid may be required. (All hydrochloric acid must be expelled before beginning the regular treatment.) The operator is expected to recognize such cases and apply the remedy. He is cautioned, however, to be very careful about modifying the method except from actual necessity. Not that improvements are not possible, but it has been the writer's experience that most of the failures result either from inattention to details or the introduction of supposed improvements by the operator.

#### DESCRIPTION OF THE METHOD.

*Standard Ferrocyanide Solution.*—Dissolve 22 grams of potassium ferrocyanide crystals in water and dilute to 1 liter. Standardize as follows: Weigh carefully about 100 mg. of pure zinc and dissolve in 6 cc. of strong hydrochloric acid, using a 400 cc. beaker. Then add about 10 grams of ammonium chloride and 200 cc. of boiling water. Titrate with the ferrocyanide solution until a drop, when tested on a porcelain plate with a drop of a strong solution of uranium nitrate, shows a brown tinge. About 20 cc. of ferrocyanide will be required, and accordingly nearly this amount may be run in rapidly before making a test, and then the titration finished carefully by testing after each additional drop. Instead of using a single drop of the zinc solution for the test, the reaction is much sharper if several drops are placed in a depression of the plate and tested with a single drop of a strong uranium solution. As this is near the end of the titration the amount of zinc lost thereby is insignificant. As soon as a brown tinge is obtained, note the reading of the burette and then wait a minute or two and observe if one or more of the preceding tests do not also develop a tinge. The end-point is usually passed by a test or two and the burette reading must be accordingly corrected. A further correction must be made for

the amount of ferrocyanide required to produce a tinge under the same conditions when no zinc is present. This is only 1 or 2 drops. One cc. of the standard solution will equal about 0.005 gram of zinc, or about 1 per cent. when 0.5 gram of ore is taken for assay.

*Assay of Ores.*—To 0.5 gram of ore in a 250 cc. pear-shaped flask, add about 2 grams of potassium nitrate and 5 cc. of strong nitric acid. Heat until the acid is about half gone and then add 10 cc. of a cold saturated solution of potassium chlorate in strong nitric acid and boil to complete dryness. It is usually necessary to manipulate the flask in a holder over a naked flame to avoid loss by bumping. The boiling may be conducted rapidly, and towards the end it is best to heat the entire flask so as to expel every trace of liquid. The potassium nitrate serves simply as a diluent of the dry residue and insures the completeness of the subsequent extraction of the zinc. Cool sufficiently and add 30 cc. of a prepared ammoniacal solution and heat to boiling. This solution is made by dissolving 200 grams of ammonium chloride in a mixture of 500 cc. of strong ammonia water and 350 cc. of water. Boil the contents of the flask very gently for about two minutes and then filter through a 9 cm. filter and wash with a hot solution of ammonium chloride containing about 100 grams of the salt and 50 cc. of strong ammonia water to the liter. Collect the filtrate in a 400 cc. beaker. The insoluble residue should be completely disintegrated and any ferric hydroxide present should appear of a fine sandy nature. Place a bit of litmus paper in the filtrate (not necessary if much copper is present), and neutralize carefully with hydrochloric acid, finally adding 6 cc. of the strong acid in excess. Dilute to about 150 cc. and add 50 cc. of a cold saturated solution of hydrogen sulphide. Heat nearly to boiling and the solution is ready for titration. If more convenient, or apparently advisable, pass a current of hydrogen sulphide gas through the hot solution diluted to 200 cc. Copper and cadmium, which are interfering metals, are thus precipitated. Unless in large amount they need not be filtered off. Practically no zinc is precipitated with the copper under these conditions and the discoloration of the liquid by even 10 per cent. of copper does not badly mask the uranium test. Titrate the

hot solution as follows : Pour off about one-third and set it aside in a beaker. Titrate the remainder, more or less rapidly, according as much or little zinc is indicated, until the end-point is passed, using the uranium indicator as in the standardization. Now add the greater part of the reserved portion and continue the titration with more caution until the end-point is again passed. Finally add the last of the reserved portion and finish the titration carefully, ordinarily two drops at a time. Make corrections of the final reading of the burette precisely as in the standardization. The true end-point is always slightly passed, and, after waiting a minute, it is usually sufficient to deduct for as many drops as show a brown tinge and one test additional.

*Notes.*—When precipitating with hydrogen sulphide it is a matter of considerable importance to have the solution of a definite degree of acidity. Cadmium and copper are to be precipitated, while it is better to retain lead in solution and not unnecessarily blacken the liquid with its sulphide. If there is enough acid to prevent the precipitation of its sulphide the lead will not interfere in the titration. On the other hand too much acid will prevent the precipitation of the cadmium. It will not come down from a boiling hot solution containing 5 per cent. of strong hydrochloric acid. It is readily precipitated from a 3 per cent. solution while lead is not, if the liquid be nearly boiling. It is therefore recommended to have an excess of 6 cc. of strong hydrochloric acid in the final bulk of 200 cc. of solution.

Arsenic, when present in large amount, sometimes makes trouble by retaining iron in the ammoniacal solution. No attention need be paid to arsenic unless its presence in excess is thus indicated. In such a case begin anew and give the ore a preliminary treatment as follows :

To 0.5 gram of ore in the flask add 10 cc. of strong hydrochloric acid and 1 cc. of bromine. Warm very gently for several minutes to decompose the ore without loss of bromine and then boil rapidly to complete dryness. The arsenic will thus be sufficiently expelled. Now add the potassium nitrate and nitric acid and proceed in the usual manner.

In the case of ores that are free from cadmium, or where cadmium may be neglected, the copper may be readily precipitated without the use of hydrogen sulphide as follows : After neutral-

izing the ammoniacal filtrate from the insoluble residue, acidify with an excess of 10 cc. of hydrochloric acid and add about 30 grams of granulated test lead. Heat nearly to boiling and stir the lead about until all the copper is precipitated. Now dilute to 200 cc. and titrate as described, without removing the lead and precipitated copper.

DENVER, COLORADO, February 20, 1900.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 21.]

### A NEW BRIDGE ARRANGEMENT FOR THE DETERMINATION OF ELECTROMOTIVE FORCE BY AID OF THE LIPPMANN ELECTROMETER.

BY J. LIVINGSTON R. MORGAN.

Received February 3, 1900.

THE two-bridge arrangements given by Ostwald<sup>1</sup> for the measurement of electromotive force by the aid of the Lippmann electrometer are the only two at present in use for primary cells. When an accumulator is used, it is only necessary to connect it through a meter of manganine wire and to compensate the cell to be measured by a fraction of the source taken off from the wire by a sliding contact.<sup>2</sup> If a primary cell were used in this way the results would not be accurate, owing to the decrease in the electromotive force of the cell due to the small resistance of the wire (50 ohms at most). Of the two methods in which primary cells may be used as a source, we may say that each is good for its purpose but that neither is of general utility. The method using the sliding contact as already described for an accumulator necessitates the use of a spool at one end of the bridge wire, which contains thirteen times the resistance of the bridge wire. In this way the cell is connected through 700 ohms ( $14 \times 50$ ) so that its electromotive force remains constant during the operation. By this, however, the drop in potential at the ends of the wire, with a Leclanché cell (1.4 volts), is only 0.1 volt, so that nothing larger than that can be measured, unless some elaborate device is provided by which another known electromotive force may be placed against the one to be

<sup>1</sup> Händ- und Hilfsbuch zur Ausführung physico-chemischer Messungen, 252-253.

<sup>2</sup> Ostwald: Grundriss der allgemeinen Chemie, 3d Ed., 434 (1899).

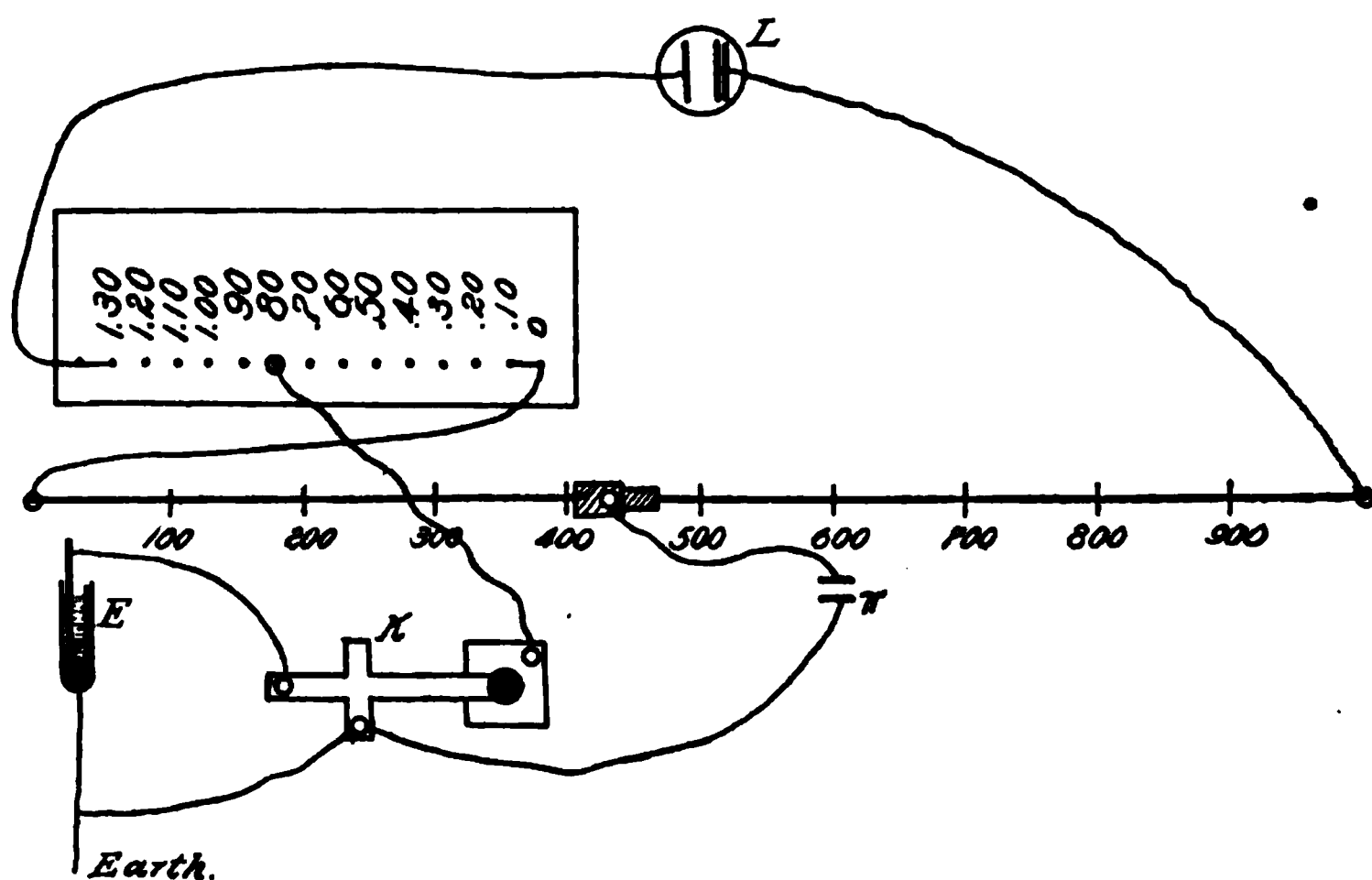
measured so as to make the difference between the two less than 0.1 volt. The accuracy of the arrangement, however, is great, for each millimeter represents 0.0001 volt if the electrometer is sufficiently delicate.

In the other method the cell is closed through a resistance box of 1000 ohms provided with nine coils of 100 ohms and ten of 10 ohms each. If the Leclanché cell is cut down to one volt by a suitable resistance, then each of the 10-ohm coils represents 0.01 volt, while each of the 100-ohm coils represents 0.1 volt. By means of two plugs, any fraction of the 1 volt may thus be placed against the electromotive force to be measured until it is compensated. Thousandths of a volt may be approximated by the movement of the meniscus of the electrometer in opposite directions, caused by the connection first to a 10-ohm coil which is just too high, and then to one which is just too low. This, however, is not to be used with very delicate electrometers for 0.01 volt may cause the meniscus to go out of the field. By the box method, then, it is possible to measure any electromotive force, even above 1 volt if a battery of 1-volt cells is at hand, with an accuracy of 0.01 volt and to approximate to 0.001 volt.

We see then that the two methods separately give satisfactory results, but that it is inconvenient, to say the least, to measure anything above 0.1 volt, with an accuracy of more than about 0.002 volt. The object of this paper is to describe a method which can take the place of both those described, and measure directly, if the electrometer is delicate enough, any electromotive force with an accuracy of 0.001 volt, and can also be used at any time for rougher work just as conveniently as the box method.

The current goes first through a box in which there are 13 coils of wire and then through a bridge wire of manganine (1 meter  $\times$  0.1 mm., resistance 50 ohms). Each of the 13 coils is of the same resistance as the wire on the bridge and may be made up of an equal length of the same wire properly insulated. On the wire there is a slider which is always in contact with the wire, while any number of the 13 coils can be brought into use in the same way as in the case of the box already mentioned. By this arrangement we have what is practically a bridge 14 meters

long of which the one meter laid out can be made any fourteenth from 1 to 14. The wire from the plug on the coils and the one from the sliding contact are treated just as those on the box are (see figure). To make a determination, the slide on the wire is placed at one end and the plug connected with the coils is moved until one post gives too great an electromotive force while the one next below it gives too small a one. The plug is then left on this latter and the sliding contact on the bridge wire



is moved until the meniscus in the electrometer is motionless when the key is pressed. To the number opposite the coil, is then added the same number of ten-thousandths as there are millimeters in the reading on the bridge. This number when multiplied by the total drop of potential at the connections to the Leclanché gives the value in volts. Possibly the use of a storage cell in the way described is to be preferred; although these cells are uncertain as a rule in their results, still this method just described has received a good trial and can be recommended whenever a primary cell is to be used.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL AND APPLIED  
CHEMISTRY, UNIVERSITY OF MICHIGAN.]

## THE THERMOCHEMISTRY OF IRON AND STEEL.

[A WITHDRAWAL.]

BY E. D. CAMPBELL.

Received February 24, 1900.

IN 1897 I published in connection with Mr. F. Thompson an article entitled "A Preliminary Thermochemical Study of Iron and Steel."<sup>1</sup> In this article some of the results given were so unusual, that it was deemed desirable to continue the work along the same lines of investigation. The work was taken up again in the autumn of 1897 by Mr. W. E. Hartman. The first experiments undertaken were to verify the results reported in our first paper as having been obtained by Mr. Thompson. Mr. Hartman was unable to duplicate the results obtained by Mr. Thompson and as a result of this I published "A Correction," in this Journal.<sup>2</sup>

During the past two years my three assistants, Messrs. W. E. Hartman, Carl Sundstrom, and E. C. Champion have worked independently in an effort to explain the very unusual results reported in our first paper. Our efforts have been towards eliminating the sources of error as much as possible; to this end the calorimeter employed has been improved in many of its mechanical details, the time of solution has been reduced to usually less than four minutes. The rate of loss by radiation for each 0.1° has been determined as well as the slight gain in heat due to oxidation of cuprous chloride by dissolved air. With the most careful manipulation the difference between duplicate determinations could be kept down below 1 per cent. of the observed amount.

The first experiments undertaken were to determine the influence of the amount of free hydrochloric acid in the solution of ammonium cupric chloride employed. An interesting fact was developed at this point; it was found that if pure carbide of iron, (CFe<sub>3</sub>)<sub>n</sub>, isolated by electrolysis from annealed steel, was added to neutral ammonium copper chloride there was little or no action, the thermometer in the calorimeter rising less than 0.01° C. in five minutes; if, however, the ammonium copper chloride solution

<sup>1</sup> This Journal, 19, 754.

<sup>2</sup> *Ibid.*, 20, 78.

contained 0.09 per cent. of free hydrochloric acid, there was marked action, and with 0.46 per cent. of free hydrochloric acid, solution of 1 gram of carbide was complete in two minutes.

Other experiments were made with increasing amounts of free hydrochloric acid up to 4 per cent., the amount used in our previous work, and although it was found that some free hydrochloric acid is necessary in order to obtain complete and rapid solution, the amount of free acid up to 4 per cent. did not appreciably influence the amount of heat evolved; practically all of the iron was dissolved by its reaction with cupric chloride and not by direct solution in hydrochloric acid. The solution finally adopted for all of the later work contained 0.84 per cent. of free hydrochloric acid.

The difficult solubility of carbide of iron in neutral ammonium cupric chloride will easily account for the results obtained by Osmond quoted in our first paper. These results go to show that if steel be quenched or cold-rolled the heat of solution is thereby markedly increased. The effect of heating and quenching steel as well as of cold-rolling is to render the carbide much more easily soluble in neutral solution than when existing in annealed metal.

The results of the experiments carried on during the past two years by Messrs. Hartman, Sundstrom, and Champion have agreed with each other within the limits of experimental error. These results all go to prove that the heat of solution of steel determined in slightly acid ammonium copper chloride is not varied at the outside more than 2 per cent. by variation in the heat or mechanical treatment of the sample nor by variations in chemical composition within the limits of ordinary steel.

In view of these later experiments it must be acknowledged that the results reported in our first paper have no foundations in fact, and I would therefore request that they be considered, if possible, as withdrawn.

I regret that results of experimentation which have not been confirmed by a second worker, should have been published from this laboratory.

ANN ARBOR, MICH., February 10, 1900.

[EDITORIAL NOTE: It would be unfair to print the above without reminding the reader that Dr. Campbell's eyesight was destroyed several years since in a laboratory accident, and in consequence he has since then been entirely dependent upon others in this respect].



[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION  
OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

## FOREIGN COLORING-MATTER IN MILK.

BY ALBERT E. LEACH.

Received March 15, 1900.

**T**HE employment of artificial color by dishonest dealers to improve the appearance of milk has been practiced for many years, and while by no means as prevalent now as formerly, by reason of the stringent laws passed by various states regulating the sale of milk, the practice even to-day is by no means rare. Even in Massachusetts, which of all states is foremost in prosecuting the milk laws, artificially colored milks are occasionally found. Statistics of the Massachusetts State Board of Health show that out of 23,098 samples of milk collected throughout the state and analyzed during five years (from 1894 to 1898 inclusive), 151 samples or 0.6 per cent. were found to contain foreign coloring-matter. Of these samples, about 88 per cent. contained annatto, approximately 10 per cent. were found with an aniline orange, and about 2 per cent. with caramel.

Until comparatively recently, annatto was employed almost exclusively for this purpose. Caramel is least desirable of all the above colors from the point of view of the milk dealer, in that it is difficult to imitate with it the natural milk color by reason of the fact that the caramel color has too much of the brown and too little of the yellow in its composition. Annatto, on the other hand, when judiciously used and with the right dilution, gives a very rich, creamy appearance to the milk even when watered, which accounts for its popularity as a milk adulterant. Of late, however, the use of an orange aniline has been on the increase, and so far as a close imitation of the cream color is concerned, it is quite as efficient as annatto.

It is unfortunate for the milkman that artificial color of any kind is not analogous to the natural color of milk, which confines itself so largely to the cream. The artificial color, on the contrary, is dissipated through the whole body of the milk, so that when the cream has risen in a milk thus colored, the underlying layers, instead of showing the familiar bluish tint of skimmed milk, are still distinctly tinged below the layer of the fat, espe-

cially if any considerable quantity of the color has been used. This distinctive appearance is in itself often sufficient to direct the attention of the analyst to an artificially colored milk in the course of handling a large number of samples.

The addition of artificial color to milk is in most instances employed as a means of covering up evidences of watering, but this is not true in all cases. About 95 per cent. of the milks found colored in Massachusetts show, on analysis, the fraudulent addition of water. On the other hand, an orange aniline color was found by the writer in a milk containing over 17 per cent. of total solids, a conviction being secured on this case in court.

As to the nature of the orange aniline preparations employed for coloring milk, a few samples of these commercial "milk improvers" have fallen into the hands of the Department of Food and Drug Inspection of the Massachusetts Board of Health, and have proved, on examination, to be mixtures of two or more members of the diazo compounds of aniline. A mixture of what is known to the trade as "Orange G" and "Fast Yellow" gives a color which is practically identical with one of these preparations secured from a milk dealer and formerly used by him.

For purposes of prosecution or otherwise the generic name of "aniline orange" has been applied to this class of dyes in milk, and whatever particular mixture has been employed to make up the color, the tests which are given below have never failed to detect it when present in the milk.

The general scheme employed by the writer for the examination of milk samples suspected of being colored is as follows: About 150 cc. of the milk are curdled by the aid of heat and acetic acid, preferably in a porcelain casserole over a Bunsen flame. By the aid of a stirring rod, the curd can nearly always be gathered into one mass, which is much the easiest method of separation, the whey being simply poured off. If, however, the curd is too finely divided in the whey, the separation is effected by straining through a sieve or colander. All of the annatto or of the aniline orange present in the milk treated would be found in the curd, and part of the caramel. The curd, pressed free from adhering liquid, is picked apart, if necessary, and shaken with ether in a corked flask, in which it is allowed to soak for

several hours or until all the fat has been extracted and with it the annatto. If the milk is uncolored, or has been colored with annatto, on pouring off the ether the curd should be left perfectly white. If, on the other hand, aniline orange or caramel has been used, after pouring off the ether the curd will be colored more or less deeply depending on the amount of color employed. In other words, of the three colors annatto, caramel, and aniline orange, the annatto only is extracted by the ether. If caramel has been used, the curd will have a brown color at this stage; if aniline orange, the color of the curd will be a more or less bright orange.

The ether extract, containing the fat and the annatto, if present, is evaporated on the water-bath, the residue is made alkaline with sodium hydroxide and poured upon a small, *wet* filter, which will hold back the fat and, as the filtrate passes through, will allow the annatto, if present, to permeate the pores of the filter. On washing off the fat gently under the water tap, all the annatto of the milk used for the test will be found to have been concentrated on the filter, giving it an orange color, tolerably permanent and varying in depth with the amount of annatto present. The confirmatory test for annatto with stannous chloride may afterward be applied to the colored filter, producing the characteristic pink color.

The fat-free curd, if colored after the ether has been poured off, is examined further for caramel or aniline orange by placing a portion of the curd in a test-tube and shaking vigorously with concentrated hydrochloric acid. If the color is caramel, the acid solution of the colored curd will gradually turn a deep blue on shaking, as would also the white fat-free curd of an uncolored milk, the blue coloration being formed in a very few minutes, if the fat has been *thoroughly* extracted from the curd; indeed it seems to be absolutely essential for the prompt formation of the blue color in the acid solution that the curd be free from fat. Gentle heat will hasten the reaction. It should be noted that it is only when the blue coloration of the acid occurs in connection with a *colored* curd that caramel is to be suspected, and if much caramel be present the coloration of the acid solution will be a brownish blue. If the above treatment indicates caramel,

it would be well to confirm its presence by any of the usual tests on a fresh sample of the milk.<sup>1</sup>

If the milk has been colored with aniline orange, the colored curd, on applying the strong hydrochloric acid in the test-tube, will *immediately* turn pink. In the case of the caramel, the color of the curd itself remains unchanged, the solution only turning blue and that gradually; on the contrary with the aniline orange the curd itself takes the pink color the moment the acid touches it. If a large amount of the aniline orange has been used in the milk, the curd will sometimes show the pink coloration when hydrochloric acid is applied directly to it, before treatment with ether, but the color reaction with the fat-free curd is very delicate and unmistakeable.

#### SUMMARY OF SCHEME FOR COLOR ANALYSIS.

Curdle 150 cc. milk in casserole with heat and acetic acid. Gather curd in one mass. Pour off whey, or strain if curd is finely divided. Macerate curd with ether in corked flask. Pour off ether.

##### Ether Extract.

Evaporate off ether, treat residue with NaOH and pour on wetted filter. After the solution has passed through, wash off fat and dry filter, which if colored orange, indicates presence of annatto.

(Confirm by  $\text{SnCl}_2$ ).

##### Extracted Curd.

(1) *If Colorless.*—Indicates presence of no foreign color other than in ether extract.

(2) *If Orange or Brownish.*—Indicates presence of aniline orange or caramel. Shake curd in test-tube with concentrated hydrochloric acid.

If solution *gradually* turns blue; indicative of caramel. (Confirm by testing for caramel in whey of original milk.)

If orange curd *immediately* turns pink; indicative of aniline orange.

## THE REPEATED USE OF THE DOUBLE CHLORIDE OF COPPER AND POTASSIUM FOR THE SOLUTION OF STEEL OR IRON IN ESTIMATING CARBON.<sup>2</sup>

BY GEO. WM. SARGENT.

Received March 30, 1900.

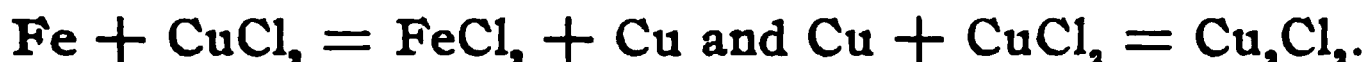
IN the *Chemical News*, Vol. 79, p. 169, which appeared April 14 of last year, there is an article headed: "The Estimation of

<sup>1</sup> See Nineteenth Annual Report of the Mass. State Board of Health (1887), p. 183.

<sup>2</sup> Read at the March meeting of the Philadelphia Section of the American Chemical Society.

Carbon in Steel; Apparatus and Materials," signed J. T., in the course of which, it is stated, that the copper ammonium chloride may be reused as many as eight times, provided it is oxidized by drawing air through it after each solution, and provided the practice of allowing the sample to dissolve over night, is adopted. After the operation had been repeated four or five times, there was a decided decrease in the rate of solution and the speed of filtering, therefore it was practicable to use it successively but three or four times, unless the solution of the drillings was made in neutral copper ammonium chloride by shaking in a stoppered flask, when upon removing the carbon and oxidizing, the clear green liquid could be filtered from the iron oxide and reused *ad infinitum*.

Copper potassium chloride, owing to its freedom from organic matter, has supplanted the ammonium salt. Most chemists use the former in a hydrochloric acid solution,<sup>1</sup> when by the aid of a stirring machine, the drillings are dissolved in less than an hour. The reaction is expressed in the following equation:



If now the cuprous chloride be oxidized to cupric, there is no reason why the double chloride solution should not be used repeatedly until the accumulated iron salts become too great. As stated above, this has been done, but the time consumed in oxidizing by a current of air was too long,—several days of an almost continuous current of air through a liter of the acid double chloride failed to completely oxidize the copper salt. The source of my air current was a filter pump, making the waste of water very considerable.

The oxidation was then attempted by the electric current using a cell such as is used for electrolytic oxidations. The result was fairly satisfactory, 3 quarts being oxidized in two days' time; but both these methods yield the cupric chloride at the expense of the hydrochloric acid:

$\text{O} + 2\text{HCl} + \text{Cu}_2\text{Cl}_2 = \text{H}_2\text{O} + 2\text{CuCl}_2$ , and  $2\text{HCl} + \text{Cu}_2\text{Cl}_2 = \text{H}_2$ ,  
at the cathode and cupric chloride at the anode. Not knowing the quantity of acid consumed in the oxidation, without keeping careful account of the drillings and solution used, it would be

<sup>1</sup> See "The Chemical Analysis of Iron," by Blair.

difficult to tell just how much acid should be added after each oxidation in order to have the double chloride of the proper strength for the next solution. Again the chlorine formed at the anode would attack it. Therefore, I decided to try the effect of chlorinating the solution direct.

The result has been most agreeable. At the present time we have three bottles of 3 quarts' capacity; in the one, the filtered double chloride ready for the solution of the drillings is kept; the second receives the undiluted filtrate from the carbon, while the third, filled with the filtrates, stands in the corner of the hood with a current of chlorine gas passing through it. It requires just a day to chlorinate 3 quarts, and that is about the amount consumed each day. When chlorinated the solution, instead of being of a dirty brown, has almost the original color of copper potassium chloride. After standing over night in the hood and being filtered, the objectionable odor of chlorine is gone and the solution is again ready for use. The chlorinated double chloride is more energetic in its solvent action. In some instances the solution of the drillings has been accomplished in fifteen minutes.

As many as eleven solutions have been made with one quantity of the double chloride, and the time required for the eleventh solution and filtration was very little longer than for the first.

The following results were obtained by the successive use of the same solution :

Number of sample.	Carbon. Per cent.	Number of times the double chloride solution had been previously used.
17 .....	0.864	None
" .....	0.864	1
1922 .....	0.605	None
" .....	0.614	2
1930 .....	0.755	None
" .....	0.752	3
1942 .....	0.410	None
" .....	0.411	4
1944CX .....	1.608	None
" .....	1.614	6
1991 .....	0.385	None
" .....	0.384	7
1969 .....	0.613	None
" .....	0.615	11

The saving effected by reusing the copper potassium chloride solution is no inconsiderable amount, especially where much of the salt is used. Roughly estimating, 1 pound of black oxide of manganese, and 1.5 pounds of hydrochloric acid, are sufficient to reconvert 3 quarts of the double chloride, worth about \$1.00.

LABORATORY OF THE CARPENTER STEEL CO.,  
READING, PA., March, 1900.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF  
APPLIED SCIENCE, No. 33.]

## ON THE DETERMINATION OF CARBON AND HYDROGEN BY COMBUSTION IN OXYGEN USING COPPER OXIDE.<sup>1</sup>

BY CHARLES F. MABERY AND WILLIAM R. CLYMER.

Received March 15, 1900.

IN a former paper<sup>2</sup> on combustion with copper oxide it was stated that some experiments were in progress to determine the conditions of efficiency, and limits of accuracy when applied to the analysis of oils containing only carbon and hydrogen.

In the long and tedious experience in the analysis of the great number of hydrocarbons that have been under examination in this laboratory, there have been ample opportunities to observe the working details in the hands of a large number of operators who have served at different times as assistants.

The difficulties in the way of securing results with oils containing only carbon and hydrogen, that will calculate closely to 100 per cent., are much greater than with substances containing smaller proportions of these elements, and require great skill and patience on the part of the operator.

Our experience shows that copper oxide is reliable after it has been brought to a constant condition by blank trials. The gases that are evolved in the combustion of some of the hydrocarbons require the highest temperature in presence of oxygen that can be brought to bear, without too great strain on the combustion tube.

The first essential is a drying apparatus that will remove water and carbon dioxide from air and oxygen, and remain in good condition without too frequent renewal. The apparatus now in

<sup>1</sup> The work described in this paper formed the subject of a thesis by Mr. Clymer for the Degree of Bachelor of Science.

<sup>2</sup> This Journal, 20, 510.

use in this laboratory which does not need renewal oftener than once in a year or two, consists of two pieces of combustion tubing 1.75 meters long, with a bend 30 cm. from one end, with an angle of about  $105^\circ$ , and placed on the wall in front of the combustion furnaces. One of these tubes for air and another for oxygen are nearly filled with broken glass and concentrated sulphuric acid. A second set of tubes are filled to the same extent with glass and a 40 per cent. solution of potassium hydroxide, one for air and another for oxygen. Air is supplied from a large iron tank under water pressure and the flow is regulated by a mercury seal. Oxygen is supplied from a smaller tank under water pressure regulated by an overflow.

For absorbing water from combustion, there is no more convenient nor efficient means than concentrated sulphuric acid. One point must be borne in mind and that is the retention of carbon dioxide by the acid. Since it is well known that concentrated sulphuric acid dissolves carbon dioxide to the extent of 75 per cent. of its volume, some experiments were made to ascertain just the conditions necessary to avoid retention in analysis.

In one experiment dry carbon dioxide was passed for one hour through 2 cc. of the acid in a U-tube, just sealed by the acid. Then dry air was passed through the acid for two hours, when the tube was found to have gained 1 milligram in weight. At the end of another hour the gain was reduced to 0.0008 gram, and at the end of the third hour the weight was just the same as at the beginning of the experiment.

In a second experiment conducted in the same manner the original weight was reached in two and one-half hours. In a third experiment a larger sulphuric acid tube was used containing 7 cc. of the concentrated acid. After passing carbon dioxide for one-half hour and air for one hour and fifteen minutes the gain in weight was 0.0075. In continuing the passage of air at the rate of 500 cc. per hour for different lengths of time the following results were obtained.

Minutes.	Increase.
15	0.0058
15	0.0047
15	0.0037
1 hour	0.0029
1 "	0.0018
1 "	0.0018
1 "	0.0001



It was, therefore, only after air had been passed five hours that the weight was reduced to the original. In a third experiment a potash bulb was placed in front of the sulphuric acid tube, and carbon dioxide was passed one hour, and air for one hour. The potash bulb was now attached and the gain in weight (with air) compared with the loss in the acid tube.

Hour.	Loss in acid tube.	Gain in potash tube.
I	0.0014	0.0014
I	0.0008	0.0007
I	0.0005	0.0005
I	0.0002	0.0002
I	0.0000	0.0001

In a fourth experiment, carbon dioxide was passed for one hour through 2 cc. of acid, then air for one hour, then air for one hour more and weighed; the gain in weight was 0.0007 gram. Carbon dioxide was then passed for one hour and air for another hour, then at the end of a second hour the weight was 0.0004 gram. In three repetitions the gains were respectively 0.0006, 0.0004, and 0.0006 gram showing that passing air the same length of time leaves the same weight of carbon dioxide in the acid. These experiments indicate that when a small volume of acid, 2 to 3 cc., is used with the large volume of oxygen and air used to expel carbon dioxide from the tube, very little of the gas remains dissolved in the acid. But with larger volumes of the acid there is danger of retention of carbon dioxide.

In testing the capacity of sulphuric acid to retain moisture, moist air was passed through 2 to 3 cc. of the acid at the rate of 1100 cc. per hour for four hours. At this rate the bubbles cannot be counted. In front of the sulphuric acid tube was placed a high tube filled with phosphorus pentoxide but there was no gain in the latter tube. There is therefore no danger of loss in water if sulphuric acid is used. The only value of this experiment was to ascertain the conditions since Morley showed several years ago that sulphuric acid is a most efficient drying agent. The form of sulphuric acid tube we have used for several years has a bulb for collecting the greater part of the condensed water which is poured out after weighing. The forward bend of the U is 10 cm. in height from the bottom and a side tube is attached for connection to the potash bulb. When containing 3 cc. of concentrated acid, and 0.2000 gram water is weighed in each

combustion, the tube may be safely used without replacing the acid in ten or twelve combustions and probably longer. That sulphuric acid is preferable to calcium chloride has frequently been shown, since the best fused calcium chloride may contain basic chloride which retains carbon dioxide. It was shown by Winkler<sup>1</sup> that lime in the chloride cannot be completely saturated by carbon dioxide, since the inside of the granules remain caustic for a long time.

It is doubtful whether there is a more convenient apparatus than the Geissler potash bulb for the absorption of carbon dioxide, especially if the substance analyzed consists, for the most part, of carbon and hydrogen. There is no danger of loss of carbon dioxide if the solution of  $33\frac{1}{3}$  per cent. potash be not used in more than four or five analyses. But there is danger of loss of moisture from the potash bulb unless care is taken to prevent it.

Some experiments were made to ascertain the conditions of safety. In one experiment the calcium chloride tube in front of the potash bulb was filled with freshly fused calcium chloride, broken to the size of grains of rice. Air was passed through at the rate of 550 cc. per hour with no loss in weight of the potash bulb, and the result was verified by placing a sulphuric acid tube in front of the calcium chloride tube which showed no gain in weight. Any faster rate than this showed a loss in the potash bulb and a corresponding gain in the sulphuric acid tube. On replacing the granular calcium chloride with other more finely ground, in a slightly longer tube, and passing air at the rate of 1050 cc. an hour, or 120 bubbles a minute, there was no change in weights. With a calcium tube of common length, 6 cm., a rate of 880 cc. per hour caused a loss of 0.0004 gram in the potash bulb and a gain of 0.0005 gram in the sulphuric acid tube. It is therefore safe to pass 500 cc. per minute through a tube filled with freshly fused finely granular calcium chloride. Such calcium chloride may be used in a considerable number of analyses. This rate can not be exceeded in the combustion of oils that are in part or all volatile without decomposition, or that yield gaseous products in burning. But this rate is in any sense in excess of the rate of evolution of gas from the combustion, since the carbon dioxide is, for the most part, immediately absorbed as

<sup>1</sup> *Ztschr. anal. Chem.*, 545, 1882.

soon as it meets the potash solution. By replacing the fused calcium chloride with phosphorus pentoxide, there was no loss even when the rate exceeded 1000 cc. per hour, or 120 bubbles a second. But the oxide offers no advantages over the fused chloride in ordinary analysis.

In preparing for a long series of combustions a combustion tube should be selected that promises to stand 50 to 100 analyses, since it requires a long time to get the tube and its contents and connections in good working order. A long time is required to remove all the volatile impurities from the best copper oxide, and the moisture from the tube and oxide. Rubber stoppers are the only means for satisfactory connections, but before they become constant in weight probably some of the sulphur must be volatilized and moisture expelled. It is therefore necessary to test carefully all parts of the apparatus by means of blank experiments in the beginning, and even after the apparatus becomes constant it is well occasionally to apply a blank test.

In conducting analyses of such bodies as the high-boiling constituents of petroleum, the closest attention to details is necessary. The tube must be as hot as it will stand, and yet not hot enough to lessen its durability, on account of the labor involved in getting it in good condition. If the combustion tube be filled with oxygen before the substance is inserted and the rate of volatilization be carefully controlled, any hydrocarbon may be burned in a furnace with 20 burners. Many analyses were lost before these conditions were fully understood. In view of the possibility that a longer combustion tube might insure complete combustion and shorten the time of the analysis, two furnaces were placed together, and a tube nearly two meters in length was used. But the results were not more satisfactory than with a tube of ordinary length.

As a general summary of what is necessary to insure desirable accuracy in such determinations, it must be fully understood at the outset that no operation in analytical chemistry demands greater precautions, closer attention to details, or more skill and patience on the part of the operator to insure results within 0.20 per cent. of the maximum 100 per cent. in substances composed solely of carbon and hydrogen, such as petroleum oils.

In view of the great amount of work that will have to be done in determining the constitution of the large number of hydrocarbons with high molecular weights in Pennsylvania, California, and other petroleums, it would be a great advantage if a method for the determination of carbon and hydrogen could be devised that would avoid the tedious routine of the present method. But with present knowledge of this subject this method is probably all that can be hoped for. The Geissler potash bulb and the sulphuric acid tube seem to be as convenient forms as can be devised and they are capable, as shown above, of retaining carbon dioxide and water with as rapid delivery as is consistent with complete combustion. Rubber corks are objectionable, but they are the only convenient and reliable means of connection available.

We have tried successfully weighing the bulbs full of oxygen, thus avoiding the expulsion of oxygen by air. But since the time necessary to carry forward all the carbon dioxide is equivalent to that necessary to displace oxygen by air, there is nothing gained by weighing the bulbs filled with oxygen. The precautions necessary to insure cleanliness of the bulbs and constant conditions of moisture and temperature in weighing must be carefully observed.

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### CIDER VINEGAR : ITS SOLIDS AND ASH.

BY R. E. DOOLITTLE AND W. H. HESS.

Received March 15, 1900.

**D**URING the past few years the question of vinegar adulteration has received considerable attention from food chemists. Heretofore the sophistication has consisted almost entirely of the sale of colored distilled vinegar for pure fermented apple juice. As distilled vinegar contains little or no solids or ash this fraud was easily detected by very simple determinations. During the year 1899, however, there appeared for sale on the markets of this state, vinegar containing the necessary amount of solids and ash required by the statute for cider vinegar; but on ordinary analysis of this the solids and ash did not have the usual appearance of solids and ash of vinegar from pure apple juice. It was to ascertain the character of these vinegars

that the investigation of the solids and ash of cider vinegar was made.

#### THE SOLIDS.

The solids of pure cider vinegar consist of glycerol, albuminous substances, gums, malic and other organic acids, and mineral matter. The solids of pure cider vinegar give no rotation with the polariscope and little or no reducing action on Fehling solution after the customary clarification with lead acetate. Pure cider vinegar gives with lead acetate a heavy, flaky, light reddish brown-colored precipitate, which carries down with it all the coloring-matter leaving the solution above clear and nearly colorless. For analysis of solids 1000 cc. of pure cider vinegar was evaporated to a thick sirup on a water-bath and this residue taken up several times with distilled water and the water evaporated off to remove acetic acid. The suspected vinegars were treated in the same manner. The appearance of the solids on evaporation should be noted. Pure cider vinegar solids have a pleasant baked apple odor and are light and foamy in appearance. The spurious vinegars gave solids like molasses in appearance and of sharp acid odor. These residues gave the following results on analysis :

	Pure cider vinegar solids. Per cent.	Apple pomace vinegar solids. Per cent.	Suspected vinegar. (1) Per cent.	Suspected vinegar. (2) Per cent.	Boiled cider. Per cent.
Reducing sugar before inversion.	0 to 14	0	42.88	56.82	61.12
"    "    after    "    .	0 to 10	0	33.36	57.04	66.45
Polarization before inversion.....	0	0	+40.7°	-31.14°	-17.9°
"    after    "    .....	0	0	+38.8°	-34.25°	-25.0°

#### THE ASH, OR MINERAL MATTER.

The ash, or mineral matter, of pure cider vinegar consists principally of potash with small amounts of sulphuric anhydride, phosphoric acid, alumina, lime, magnesia, etc. The total amount should not be less than 0.25 per cent. For analysis, 100 cc. of the vinegar are taken for the determination of the total solids and ash in the usual way. The ash is dissolved in dilute hydrochloric acid and quantitative analysis made by the usual

method. The results in the following table are given as the average composition as determined by a large number of analyses. The suspected vinegars, Nos. "1" and "2," and also the ash of vinegar made by repressing moist fermented apple pomace, are given for comparison.

	Pure cider vinegar ash. Per cent.	Apple pom- ace vinegar ash. Per cent.	Vinegar. (1) Per cent.	Vine- gar. (2) Per cent.
Calcium Oxide (CaO) . . . . .	3.40 to 8.21	4.73	4.70	37.95
Magnesium oxide (MgO) . . .	1.88 to 3.44	4.12	2.00	2.22
Potassium oxide (K <sub>2</sub> O) . . . . .	46.33 to 65.64	37.00	None	7.84
Sodium oxide (Na <sub>2</sub> O) . . . . .	Trace to trace	Trace	49.71	Trace
Sulphuric anhydride (SO <sub>3</sub> ) .	4.66 to 16.29	34.78	27.04	12.74
Phosphoric anhydride (P <sub>2</sub> O <sub>5</sub> ) .	3.29 to 6.66	9.66	0.005	1.82
Iron oxide (Fe <sub>2</sub> O <sub>3</sub> ) . . . . .	None to trace	Trace	Trace	1.60
Carbon dioxide, loss, etc. . . . .	40.44 to 0	9.61	16.54	35.83

The results of these analyses plainly showed that suspected vinegar No. 1 was composed of dilute acetic acid, glucose, and soda-ash. Suspected vinegar No. 2 was a mixture of acetic acid, boiled cider, and lime.

LABORATORY MICHIGAN DAIRY AND FOOD DEPARTMENT,  
March 12, 1900.

### NOTES.

*Test for Tin.*—I have found the blue color produced by the action of stannous chloride upon ammonium molybdate to serve as a very delicate test for tin; and have had my students use it for the last few months with very good results. In working this process one should go through the usual separation, filter off the black flakes, dissolve them in hydrochloric acid, then take a few drops of this solution and add a little water and then some ammonium molybdate. Blue color shows the presence of tin.

To determine the delicacy of the test, I used a standard solution of stannous chloride, and noticed results obtained from the mercuric chloride and ammonium molybdate tests.

Strong solution of SnCl<sub>2</sub> gives a heavy blue precipitate; with mercuric chloride a heavy white precipitate.

A solution of SnCl<sub>2</sub> containing 0.000021 gram to 1 cc. gives a deep blue color; with mercuric chloride a faint cloudiness.

A solution of SnCl<sub>2</sub> containing 0.0000042 gram to 1 cc. gives a

faint blue color with ammonium molybdate; with mercuric chloride not even a trace of cloudiness.

I find that the ammonium molybdate as prepared in the laboratory gives the best results.

ALLEN ROGERS.

Professor C. F. Mabery has sent to the Paris Exposition, at the invitation of the United States Geological Survey, 150 specimens of products from petroleum, illustrating the composition of Pennsylvania, Ohio, Canadian, California, South American, and Japanese petroleums, and specimens of nitrogen compounds from California petroleum, and sulphur compounds from Canadian petroleum. Other specimens illustrate the composition of paraffin.

### NEW BOOKS.

**DESCRIPTIVE GENERAL CHEMISTRY.** BY S. E. TILLMAN, Professor of Chemistry, Mineralogy and Geology, United States Military Academy. Second Edition. New York: John Wiley and Sons. London: Chapman and Hall. x + 429 pp. 8vo. cloth. Price, \$3.00.

This book was written to meet the requirements for a text-book on chemistry at the Military Academy at West Point. It aims to give in compact form the salient facts of chemistry that the professional soldier ought to know. The time available for the study of chemistry at the Academy is a little less than two-hundred hours, so that in order to cover the subject but a very limited amount of laboratory work can be undertaken. The chief aim therefore is to impart to the student the necessary information, rather than to make the element of mental discipline the more prominent one. Study of a text-book accompanied by recitations and experimental and explanatory lectures together with a small amount of selected laboratory work consequently make up the course pursued.

The book is divided into six chapters which are as follows: I. Essential Principles of Chemistry, pp. 1-58; II. Affinity, pp. 59-81; III. Non-metals, pp. 82-192; IV. Metals, pp. 193-310; V. Organic chemistry, pp. 311-356; VI. Applications of Chemistry, pp. 357-411. In the first chapter the general principles of chemistry are stated, while in Chapter II, the law of mass action, strength of acids and bases, theory of solution, electrolysis,

thermal chemistry, periodic law, etc., are discussed. All this is of course done very briefly, and in connection with these two chapters, in particular, the explanatory lectures mentioned above will no doubt be very essential. Chapters III and IV are not unlike chapters on the same subjects found in other texts. In the 45 pages devoted to organic chemistry only a number of groups of such compounds as are of the utmost practical importance to the particular student for whom the text is intended could be considered. The applications of chemistry in the last chapter include calorific value, explosives, fixed oils, dyeing, and the manufacture of glass, pottery, coal-gas, beer, distilled liquors, wine, bread, soap, leather, and cheese. While this chapter is devoted to practical applications exclusively, the author has not neglected to seize the opportunities of pointing out numerous practical applications in the chapters preceding.

The author has earnestly endeavored to incorporate recent discoveries and theories into his book. While his statements are generally clear, they are unfortunately not always free from inaccuracies. Only a few instances of this will here be mentioned. So on p. 69 the author neglects to point out that the assumption of electrical charges on the ions is a salient part of the theory of electrolytic dissociation, but simply adds in a footnote that the ions are probably electrically charged. On p. 71 heat of formation is confused with the thermal change that accompanies a chemical reaction. On p. 99 the statement is made that the form of the crystal is due to water of crystallization.

The book as a whole is good for the purpose for which it was written. The selection of the topics treated (upon which so much depends in a case like this) is wise; and the presentation is good considering the very condensed form necessitated. There can be no doubt that the book will meet the special needs of the students at the Military Academy better than any other textbook that is available at present.

LOUIS KAHLENBERG.

LEITFADEN FÜR DEN UNTERRICHT IN DER ANORGANISCHEN CHEMIE. BY DR. JOACHIM SPERBER. Zürich: Verlag von E. Speidel. 1899. 119 pp.

This is the first part of an extended treatise on inorganic chemistry. It treats of the usual gaseous elements, the halogens, and the non-metals. The author has applied the



inductive method to the teaching of inorganic chemistry. From simple and well chosen experiments, the fundamental principles are derived. Each set of experiments is chosen with the idea of illustrating some particular law, and is given in advance of the statement of the law itself. The laws of definite and multiple proportions, and Avogadro's law, are all established by experiment before the detailed study of the elements is begun. The order in which the separate elements are taken up is unusual. Beginning with hydrogen, the elements fluorine, chlorine, bromine, and iodine are studied, and then their hydrogen compounds. Subsequently oxygen, sulphur, selenium, and tellurium are taken up, and followed by their hydrogen compounds. Then comes the group of trivalent elements, nitrogen, phosphorus, arsenic, followed by the tetravalent carbon and silicon.

The statements in regard to the occurrence, preparation, properties, and uses of the separate elements are concise, accurate, and comprehensive. Separate theoretical considerations such as the dissociation of substances by heat, the determination of molecular weights, etc., are discussed in appropriate places, which tend to emphasize them and to show their applicability. The book contains the most recent discoveries. The illustrations are frequent, and exceptionally good.

HENRY FAY.

LEXIKON DER KOHLENSTOFF VERBINDUNGEN. VON M. M. Richter. Zweite Auflage der "Tabellen der Kohlenstoff-Verbindungen nach deren empirischer Zusammensetzung geordnet." Hamburg und Leipzig: Leopold Voss; New York: G. E. Stechert. pp. about 3100. Price, 39 Lieferungen at M. 1.80 each.

It is, apparently, impossible to secure the adoption of a uniform system of nomenclature for carbon compounds. Indeed some chemists claim, and with good reason, that complete uniformity is not desirable. It becomes, therefore, every year more difficult to be sure of finding, in chemical literature, what is known about particular compounds. The work before us furnishes a lexicon of the carbon compounds arranged in accordance with their empirical formulas. The order is, first, that of the number of carbon atoms, second, that of the number of elements, third that of the elements other than carbon in the order:

H O N Cl Br I F S P Al.....Zr.

The only exception to a rigid use of the above classification

is in the case of salts, which are given under the corresponding acids or bases. After each empirical formula is given the percentage composition for all compounds containing only carbon, hydrogen, oxygen, and nitrogen. Then follows a list of all known isomers of the given composition, giving melting-points and boiling-points, references to the literature, and finally the volume and page of the last edition of "Beilstein" where the compound is described. The number of compounds included in the work is about 75,000, while the last edition of "Beilstein" includes only 57,000.

The usefulness of the principle used for registering organic compounds is so apparent that it has been adopted for the indexes of the *Berichte* and of Liebig's *Annalen*.

The literature is fully covered to the end of 1898, and yearly supplements are promised.

A few errors have been detected, but mostly where confusion exists in the literature and a critical knowledge of the relations involved was necessary to avoid mistake. Even such errors are probably rare and will seldom cause trouble in using the work.

The author complains that the failure to give empirical formulas, on the part of many writers, has added greatly to his labors and requests that such formulas be always given. In the opinion of the writer it would be a misfortune if this request should lead to the use of fewer structural formulas. The needs and advantage of the average reader are of greater importance than the time of the lexicographer.

WILLIAM A. NOYES.

THE URINE AND THE CLINICAL CHEMISTRY OF THE GASTRIC CONTENTS, THE COMMON POISONS, AND MILK. BY J. W. HOLLAND, M.D., Professor of Medical Chemistry and Toxicology, Jefferson Medical College of Philadelphia. Sixth edition, revised and enlarged. Philadelphia: P. Blakiston's Son & Co. 49 illustrations. Cloth. Price, \$1.00 net.

This syllabus for the laboratory aims to guide the student in the chemical examinations that are of service to the physician. The methods are much the same as may be found in similar works, and, while in many instances they are well selected, they include certain methods that might better be omitted or replaced by procedures which yield results of clinical value. The brief text omits much information that would add materially to the work. It is particularly desirable to indicate more definitely to what use the results obtained by the various methods are to be

put in practice, even at the risk of adding slightly to the bulk of the text. Unfortunately misstatements are not infrequent and there is an unusual number of errors in the references.

E. E. SMITH.

ANNUAIRE DU BUREAU DES LONGITUDES, pour l'An 1900. Paris : Gauthier-Villars. 18mo. 800 pp. Price, 1.85 francs.

This handy little annual is, as its name would indicate, mostly concerned with astronomic data. The first three hundred pages are devoted to calendars, astronomic phenomena of 1900, data of all kinds concerning the sun, moon, earth, planets, stars, and comets. Then follow tables of various weights and measures, moneys, statistics of population, territory and mortality in different countries. These are followed by diverse tables, such as magnetic intensity in various parts of France ; specific gravities of solids, liquids and gases ; acoustic, optic, and electric data.

The scientific addenda contain a well-written article of thirty pages on "electric units," by A. Cornu ; an essay of over eighty pages on "dynamo-electric machines" also by Cornu, concise but satisfactorily written, and a short essay on "the new gases of the atmosphere," by Lippmann.

Many of the tables concerning physical and chemical facts are incomplete, and do not give the very best, latest determinations. In general, the French determination only is given, whenever a datum has been determined by a Frenchman, and his value stands until some other Frenchman does it better. This may be very patriotic, but it is not scientific, or good sense.

Visitors to Paris this year will be interested in the statement that "The legal time in France is that of the observatory of Paris, and is that recorded by the dials *outside* the stations, the dials *inside* the stations being several minutes later, for purely administrative reasons !"

J. W. RICHARDS.

OPTICAL ACTIVITY AND CHEMICAL COMPOSITION. BY DR. H. LANDOLT, Professor of Chemistry in the University of Berlin. Translated with the author's permission by JOHN McCRAE, Ph.D. London : Whittaker and Co.; New York : The Macmillan Company. 158 pp. Price, \$1.00.

This little book is a translation of the eighth chapter of the well-known Graham-Otto "Lehrbuch der Chemie," which has passed through several editions. This eighth chapter was contributed by Professor Landolt who is the great authority on

everything connected with the subject of the optical activity of organic compounds. The discussion in this book covers briefly the subject of optical activity in general and the relation of this activity to the composition and structure of various groups of organic compounds. It does not deal with the practical applications of polariscopic methods at all, this larger field being fully covered by the important work of the author, "Das optische Drehungsvermoegeu organischer Substanzen, und dessen praktische Anwendungen," an English translation of which is now being made by the writer of this notice.

Dr. McCrae's translation is an extremely clear and creditable one and the book will undoubtedly be found useful.

J. H. LONG.

CHEMISCH-TECHNISCHE UNTERSUCHUNGSMETHODEN. HERAUSGEGEBEN VON DR. GEORG LUNGE. Zweiter Band. 143 Abbildungen. Vierte Auflage. Berlin: Julius Springer, 1900. xii + 804 pp. Price, 16 marks.

This volume treats of Iron, by Th. Beckert; Other Metals, Metallic Salts, Dr. Pufahl; Fertilizers, Dr. O. Böttcher; Fodders, Dr. F. Barnstein; Explosives, O. Guttman; Matches, Wladimir Jettel; Gas Manufacture, Ammonium Compounds, Dr. O. Pfeiffer; Coal Tar, Dr. H. Köhler; Inorganic Colors, Dr. Gnehm. In such a wide range of subjects some unevenness in treatment is inevitable. A careful examination of the book shows that in the main, the work has been well done though there are some omissions that will surprise the reader familiar with recent practice. For example, nothing is said of the methods for the determination of phosphorus in steel depending upon the reduction of molybdenum in the yellow precipitate and its determination by permanganate. Cupric ammonium chloride only is mentioned as a solvent for iron in carbon determinations. No reference is made either to the recent improvement in Jones' reductor or to Dr. Shimer's beautiful combustion method now so widely used. There are other omissions equally serious.

Rapid methods are absolutely essential in steel laboratories where the bulk of such work is done and any treatment which, like this, fails to give them proper prominence cannot be pronounced altogether satisfactory.

In a German book it is unusual to find so many references to American improvements. The Gooch crucible, Hoskins' gaso-

line furnace, Ricketts' rubbing plate, and Jones' reductor are all mentioned and some of them figured and there are numerous references to this Journal, to the *Journal of Analytical and Applied Chemistry*, and to the *Engineering and Mining Journal*. Drown's method for silicon is described as "Verfahren von Brown."

One feature of the book deserving of notice is the reprinting of the most useful tables on separate sheets. These are placed at the end of the book to be torn out and pasted up in the laboratory if desired. The mechanical execution of the book is excellent. The third volume is promised for the middle of 1900.

E. H.

**THE GRAMMAR OF SCIENCE.** BY KARL PIERSON. Second edition revised and enlarged with 33 figures. London: Adam and Charles Black. 1900. New York: The Macmillan Co. 8 vo. xviii + 548 pp.

This is a metaphysical book written by a believer in scientific methods. It is divided into twelve chapters and an appendix. The chapters are entitled as follows: Introductory; The Facts of Science; The Scientific Law; Cause and Effect—Probability; Space and Time; The Geometry of Motion; Matter; The Laws of Motion; Life; Evolution (Variation and Selection); Evolution (Reproduction and Inheritance); The Classification of the Sciences; The mechanical execution of the book (printed by R. and R. Clark; Edinburgh) is superb.

E. H.

**ELEMENTARY CHEMISTRY FOR HIGH SCHOOLS AND ACADEMIES.** BY ALBERT L. AREY. C. E. Rochester High School. New York: The Macmillan Company. 1899. xi + 271 pp. Price, 90 cents.

There seems to be an increasing tendency to introduce chemistry into the secondary schools as a disciplinary study. This volume is offered as a text-book in elementary chemistry, and is an attempt to present the subject in such a manner as to develop the student's faculties for observation and interpretation. This is accomplished by making the book a laboratory guide as well as a text-book. Numerous questions on the text and the laboratory experiments are found throughout the book. They have been intelligently selected, and are of such a nature that they can be answered only by direct experiment or by analogy. Many statements of facts have purposely been omitted so that the student may be more impressed with the experiment. The experiments are well selected and well arranged.

The main portion of the book treats of the elementary laws, the preparation, properties, and reactions of the gases, non-metals and metals. No mention of the periodic law is made, and there is no attempt to show the striking analogies in the properties of the elements and their compounds. It is much to be regretted also that there is little mention of historical names. They are so intimately connected with the science that it seems a great pity to have dropped them almost entirely. The author has introduced the term *crith* as the weight of a liter of hydrogen. It does not aid in the understanding and must surely lead to confusion.

The last chapter of twenty-five pages treats briefly of qualitative analysis. In the reviewer's opinion this portion of the book should have been devoted to the study of the preparation of typical inorganic compounds. The prime object of many books of this class is to prepare the student to make *separations*. While this cannot be said of this volume, there will, nevertheless, be a strong tendency on the part of the student to anticipate qualitative analysis on account of its presence in the book.

With the exception of the criticisms made, the book is to be commended.

HENRY FAY.

THE THEORY OF ELECTROLYTIC DISSOCIATION AND SOME OF ITS APPLICATIONS. BY HARRY C. JONES, Associate in Physical Chemistry in Johns Hopkins University. New York: The Macmillan Company. 1900. Cloth. xii + 289 pp. Price, \$1.60.

This book contains a survey of the earlier physical chemistry, an account of the origin of the theory of electrolytic dissociation together with a presentation of the evidence supporting the same, and some of the important applications of the theory.

Every student of chemistry, physics, and biology, who is not already well acquainted with the theory of electrolytic dissociation will find this an interesting and valuable book to read. The development of modern physical chemistry is, in a large measure, intimately connected with this theory. The facts that the latter has been able to explain and to correlate are many; and above all, the importance of the stimulus it has given to research can hardly be overestimated.

In this book the theory of electrolytic dissociation is viewed in its most favorable light. It must be admitted, however, that during the last year or two, facts have begun to accumulate which

the theory cannot explain. Though these facts have developed mainly from a study of non-aqueous solutions, yet in many instances the theory finds much difficulty in explaining the facts in case of aqueous solutions, especially when quantitative data are involved. It seems at present that even before the theory of electrolytic dissociation will have found its way into regular chemical text-books, it will have undergone radical modifications from its present form, or will perhaps have been superseded by more adequate explanations. LOUIS KAHLENBERG.

VICTOR V. RICHTER'S ORGANIC CHEMISTRY OR CHEMISTRY OF THE CARBON COMPOUNDS. Edited by PROF. R. ANSCHÜTZ. Authorized translation by EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania. Third American from the eighth German edition. Vol. II. Carbocyclic and Heterocyclic Series. Philadelphia: P. Blakiston's Son & Co. 1900. 671 pp. Price, \$3.00.

The first volume of this work was reviewed last year.<sup>1</sup> About the only adverse criticism which could be made of the completed work is that the theoretical discussions are often so concise that it is almost impossible for beginners to comprehend them. It is, however, necessary, in a book of this character, to choose between a very concise style and the omission of a great deal of material which it is desirable to include. The book is, undoubtedly, much more valuable because the former alternative was chosen. The comprehensive character of the work, considering its size, is remarkable.

In discussing Ladenburg's prism formula for benzene on page 41 the author has, apparently, overlooked the fact that, since the reduction of ortho compounds gives derivatives of cyclohexane in which the substituents are combined with adjacent carbon atoms, the prism formula must be considered as positively disproved.

Professor Anschütz has availed himself of the aid of other workers who are specially conversant with particular fields and has so secured an accuracy of presentation which a single author could not hope to attain. W. A. NOYES.

AN INTRODUCTION TO PHYSICAL CHEMISTRY. BY JAMES WALKER, Professor of Chemistry in University College, Dundee. New York: The Macmillan Company. 1899. 8vo. Cloth. x+335 pp. Price, \$2.50. A number of elementary treatises on physical chemistry have

<sup>1</sup> This Journal 21, 708.



recently appeared. Although Professor Walker's book is rather more voluminous than other works on the same subject intended for beginners, it does not pretend to give a complete or even systematic survey of physical chemistry. Its main object as expressed by the author is to be explanatory and to place the student in a position to profit by the study of the larger systematic works of Ostwald, Nernst, and van't Hoff.

The book is divided into 27 chapters; and, though the enumeration is somewhat long, there is perhaps no better way to convey an idea of the contents of this treatise than to indicate the subjects of these chapters together with the number of pages devoted to each. The chapters are as follows:—Units and Standards of Measurement, pp. 1-7; The Atomic Theory and Atomic Weights, pp. 8-21; Chemical Equations, pp. 22-26; The Simple Gas Laws, pp. 27-29; Specific Heats, pp. 30-37; The Periodic Law, pp. 38-49; Solubility, pp. 50-59; Fusion and Solidification, pp. 60-72; Vaporization and Condensation, pp. 73-83; The Kinetic Theory and Van der Waals' Equation, pp. 84-96; The Phase Rule, pp. 97-116; Thermochemical Change, pp. 117-126; Variation of Physical Properties in Homologous Series, pp. 127-135; Relation of Physical Properties to Composition and Constitution, pp. 136-147; The Properties of Dissolved Substances, pp. 148-157; Osmotic Pressure and the Gas Laws for Dilute Solutions, pp. 158-168; Deductions from the Gas Laws for Dilute Solutions, pp. 169-175; Methods of Molecular Weight Determinations, pp. 176-192; Molecular Complexity, pp. 193-200; Electrolytes and Electrolysis, pp. 201-216; Electrolytic Dissociation, pp. 217-233; Balanced Actions, pp. 234-253; Rate of Chemical Transformation, pp. 254-265; Relative Strengths of Acids and Bases, pp. 266-282; Equilibrium between Electrolytes, pp. 283-295; Applications of the Dissociation Theory, pp. 296-310; Thermodynamical Proofs, pp. 311-332.

The general treatment is non-mathematical, a few thermodynamical proofs in the last chapter being the only exceptions. The book really includes nearly all the important topics usually taught in classes in physical chemistry. The absence of a chapter on photochemistry may be noted, as may also the treatment of Nernst's theory of the E. M. F. of galvanic cells. The



order in which the subjects are considered is different from the usual one. Without going into details concerning this point, it may suffice to say that the manner in which the separate chapters are written is such as to weave them together in a logical way. The author seeks to have the student connect physical chemistry with his previous chemical knowledge so as to make the new subject of real use to him.

Clearness of statement characterizes the book throughout. The relative amount of space devoted to some of the subjects is perhaps open to some criticism; so, for example, the subject of thermal chemistry is treated in ten pages. The author, however, does not intend this to suffice but directs the student to the treatise of Muir and Wilson on this subject.

In the discussion of the applications of the dissociation theory the author has wisely chosen to content himself almost entirely with a merely qualitative treatment, since the quantitative side of this subject (especially whenever it involves the combination of the law of mass action and the theory of electrolytic dissociation) leaves much to be desired.

The book is indeed an introduction to the study of physical chemistry, for a perusal of its pages will give the student a knowledge of general, fundamental facts and will lead him to further inquiry. The author is clearly not one of those who believe that the subject of physical chemistry is already in a high state of perfection and that there is but little left to do except to fill in the details. It is to be regretted that the book does not contain more references to original articles.

LOUIS KAHLENBERG.

WATER AND WATER SUPPLIES. BY DR. JOHN C. THRESH. Second revised edition. vii+438. pp. Philadelphia: P. Blakiston's Son & Co. 1900.

Although this is called the second, revised edition of this work, it is an exact reproduction of the 1896 English edition, the only revision apparent being the correction of typographical and other errors in the first edition. It is nevertheless, a convenient handbook on water supplies.

The first part of the book treats of water, its composition, properties, etc.; the various sources of water supplies, as rain, surface, subsoil, spring, deep-well, and river water; the amount

and character of the water derived from these various sources; the nature and source of the impurities that may gain access to these different waters; and analyses of water supplies derived from these various sources. Then follow several chapters on the quality of drinking-waters; the effects upon health of impure waters; the interpretation of water analyses; the pollution of drinking-water; the self-purification of rivers. The purification of water, both on the large scale and for domestic purposes is treated of in subsequent chapters.

There is also a chapter on the laws relating to water supplies as comprised in the different special acts of Parliament with reference to the powers of individuals, towns and water companies, and likewise the various restrictions which have been raised in order to maintain the purity of natural water supplies.

The information contained in the book is drawn from the large personal experience of the author and from the voluminous literature on the subject. In this respect the author has shown considerable appreciation of the experiences of American investigators, especially the pioneer work performed in the study of filtration of water and sewage by the Massachusetts State Board of Health.

In discussing the interpretation of water analyses the author states that "Although a mere analysis cannot guarantee us purity and safety, yet it very frequently can reveal to us impurity and risk. When the source of a water, upon most careful examination by an expert, is found to be free from all danger of pollution, and the chemical examination proves that the inorganic constituents are unobjectionable, both in quantity and quality, and that organic matter is absent or present in barely appreciable amount, then safety, so far as human foresight can be trusted, may be guaranteed . . . . Chemical analysis, therefore, has its use; it is only when it is made the sole arbiter between safety and risk that it is abused, and is liable to lead to errors fraught with most disastrous consequences. Let the analysis be as careful and complete as possible, but let the results always be interpreted in the light afforded by a searching examination of the source of the sample."

At the close of the chapter he says: "Bacteriological, microscopical, and chemical examinations must always be associated

with a thorough investigation of the source of the water, to ascertain the possibility of contamination, continuous or intermittent. Then, and then only, if everything be satisfactory, we may be justified in speaking of safety and of freedom from risk; but where either bacteriological, microscopical, or chemical examination is unsatisfactory, the inquiry into the history of the water must be most careful and complete, and a guardedly-expressed opinion given only after a full consideration of the bearing of the one upon the other."

It is gratifying to read such positive statements with regard to the analysis of water for sanitary purposes because it is too frequently the case that either the chemist, bacteriologist, or the microscopist, or each of these, places undue value upon his results. Quite frequently all three forms of examination are necessary to form a definite idea as to the relative purity of a water. The author's long experience as an analyst and medical officer of health renders his opinion in this respect all the more valuable.

D. H. BERGEY.

**A TREATISE ON CRYSTALLOGRAPHY.** BY W. J. LEWIS, M.A., Professor of Mineralogy in the University of Cambridge. Cambridge University Press. 8mo. 604 pp. Price, 14 shillings, net.

This is one of the most pretentious treatises on this subject which has appeared in the English language. The important, and, from a crystallographic standpoint, historic chair which the writer holds, has naturally given to his work a decidedly conservative tone, from which many modern students will differ.

There are ten chapters (140 pages) dealing with the general geometric properties of crystals; seven chapters (300 pages) on the different systems; one chapter (100 pages) on twin crystals; and two short chapters on "divers notations" and goniometers, respectively.

The chapter on the formation of crystals is fragmentary and altogether too brief. The same is to be said of the chapter on "the law of constancy of angle." "Symmetry" is introduced clumsily but illustrated satisfactorily. The chapter on "axial representation" is somewhat labored; many of the points could have been just as satisfactorily proved by less cumbersome geometrical proof. The heavy Euclidean methods are tedious. The chapter on zone-indices and relations of zones is well stated, and,

didactically, is perhaps the best chapter in the book ; the chapter on the " anharmonic ratio " is also well done. Two chapters on crystal drawings and projections are satisfactory except for some more roundabout proofs, and the omission of all reference to gnomonic projection—an omission much to be deplored, for a projection which shows all zones as straight lines, instead of great circles, is surely worthy of the crystallographer's best attention.

The chapter on " The Systems " is unphilosophically written and, from a non-English point of view, indefensible. No attempt is made to explain clearly the philosophy of the matter. No clear proof is given why only 32 classes of forms (Groth's) are possible, and no satisfactory explanation of the peculiarities of the systems is attempted. The fact that Dr. V. Goldschmidt<sup>1</sup> has *proved* the unscientific nature of Groth's classification, and that the optical, thermal, electric as well as geometric properties of crystals all point to the six commonly accepted systems as the bases, the units, the fundamentals of crystal classification,—all this is overlooked. The old notion of making rhombohedral crystals into a seventh system is revived, although none of the physical properties of such crystals differentiate them from the hexagonal system ; and further yet, Miller's axes of reference are retained instead of substituting the Bravais, which are universally conceded as better and more logical. This is one of the worst examples of unwise conservatism in the book.

The seven chapters on the systems are thoroughly and conscientiously worked out. Particularly praiseworthy are the large number of actual specimens described as examples, most of these being descriptions of crystals in the Cambridge Museum. The concrete examples thus furnished are a great help to understanding the text, besides being valuable crystallographic data in themselves.

The long chapter on twinning is lucidly written, and enriched by drawings and data concerning many interesting specimens from the Cambridge collections. It is the best chapter in the book.

Taken altogether, it is a good exposition of old-school crystallography, with the addition of Groth's classification, rather unskillfully presented. The details of crystal forms, calculations,

<sup>1</sup> *Ztschr. Krys.*, January, 1899.

twins, etc., are well done, and the book is chiefly valuable to the advanced student for this information. For beginners, or as an introduction to the main principles of crystallography, it is unsuited, for it is not sufficiently didactic in tone nor clear in presentation, while making the primary error of misconceiving the fundamentals of crystal classification.

The paper, type and drawings are first class, the binding rather frail, and the uncut edges an abomination.

JOSEPH W. RICHARDS.

BEGINSELEN DER SCHEIKUNDE. Door M. C. SCHUYTEN. Antwerpen. 1889. pp. 110. 8 vo.

The author of this little volume, who is professor at the Institute for Higher Studies in Brussels, as well as at the Technical School of Antwerp, has prepared for elementary classes a book on the rudiments of inorganic chemistry including chemical analysis. Naturally, in so small a compass some topics have to be treated superficially; thus spectrum analysis is dealt with in one page and three lines; half a page is given to the properties useful in determining minerals, and this is followed by a table giving the names, composition and chief properties of 84 minerals.

In the preface the author explains that he has adopted the sound principle to "go from the known to the unknown." The book is excellently printed, a variety of types assisting comprehension. The few illustrations are sectional. Questions are introduced to aid teacher and pupil.

H. C. B.

THE KINETIC THEORY OF GASES. Elementary Treatise with Mathematical Appendices. BY OSKAR EMIL MEYER. Translated from the second revised edition by ROBERT E. BAYNES. London, New York, and Bombay: Longmans, Green, & Co. 1899. xvi + 472 pp. 8vo. Cloth. Price, 15 shillings.

The first German edition of this treatise appeared in 1877, the first half of the second edition in 1895, and the second half in 1899. We have in the book before us the translation of the complete second edition.

In this revised edition the general plan of the first edition has been followed. The book is divided into three parts, together with six mathematical appendices. The subjects treated are as

follows: Part I. Molecular Motion and Its Energy, pp. 3-145; Part II. The Molecular Free Paths and the Phenomena Conditioned by Them, pp. 149-296; Part III. On the Direct Properties of the Molecules, pp. 299-352. The mathematical discussions connected with the treatment of these subjects are contained in the Appendices, pp. 355-466; they make no claim to completeness. While the contents of the book are limited to the same general range of phenomena considered in the first edition, an explanation on the kinetic theory of the resistance of air and of the reaction of a jet, together with an investigation concerning the influence of the dissociation of the molecules of a vapor upon its viscosity, have been inserted.

The author deserves much credit for the manner in which he has worked up the bulky literature of the subject which has accumulated during the past two decades. The translator has provided the English speaking public with a good translation of this valuable work. He has not added anything new except a few foot-notes, but he has provided an index that is an exceedingly valuable addition to the book.

Of late, criticisms of the kinetic theory of gases have frequently been heard, and it has even been charged that the theory has outgrown its usefulness and that it has done more harm than good. Nevertheless these very critics still gladly reach out for the kinetic theory whenever it can be used to explain some of their own pet theories, particularly those relating to the analogy between gases and solutions.

English-speaking scientists, and chemists in particular, will welcome this new English edition of Professor Meyer's excellent book.

The work of the publishers is very commendable.

LOUIS KAHLENBERG.

LABORATORY MANUAL. EXPERIMENTS TO ILLUSTRATE THE ELEMENTARY PRINCIPLES OF CHEMISTRY. BY H. W. HILLYER, PH.D., Assistant Professor of Organic Chemistry in the University of Wisconsin. 200 pp. New York: The Macmillan Co. 1899. Price \$1.90.

The "book is written for the use of college students of general chemistry." The first and much the larger portion of the book, (Part I.) is devoted to the preparation and properties of the elements and their compounds; another portion (Part II;) presents a limited number of quantitative experiments for the

verification of quantitative laws: the appendix contains needful data for the students' use. In the selection of experiments the author provides for beginners, for those possessing slight familiarity with the subject, and for those who have had a satisfactory laboratory course in the preparatory school. The experiments are well chosen and graded, the directions are carefully stated, and the questions are plainly those of a painstaking teacher. The directions to the student regarding his preliminary preparation for each laboratory exercise are, in particular, excellent. The book is well printed and excellently bound.

H. P. TALBOT.

**VOLUMETRIC ANALYSIS, SPECIALLY ADAPTED TO THE REQUIREMENTS OF STUDENTS ENTERING FOR THE ADVANCED PRACTICAL CHEMISTRY EXAMINATIONS OF THE SCIENCE AND ART DEPARTMENT.** By JOHN B. COPPOCK. London: Whittaker & Co.; New York: Macmillan & Co. 12mo. pp. 92. Price, 50 cents.

The nature of this book is sufficiently indicated in the title. There is nothing contained in it worthy of special mention. It is chiefly notable for its omissions. Such books are of little value except to those who wish to pass an examination and have no further interest in the subject.

E. H.

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### BOOKS RECEIVED.

**Leitfaden für den Unterricht in der anorganischen Chemie.** Didaktisch bearbeitet von Dr. Joachim Sperber. Erster Teil. Zürich: Verlag von E. Speidel. 1899. 120 pp. Preis, M 2.40.

**A Description of Some Chinese Vegetable Food Materials and their Nutritive and Economic Value.** By Walter C. Blasdale. Bulletin No. 68, U. S. Department of Agriculture, Washington, D. C. 1899. 48 pp.

**Preservatives in Canned Foods.** Bulletin No. 165. 8 pp. **Butter Adulteration.** Bulletin No. 166. 12 pp. The North Carolina College of Agricultural and Mechanical Arts, Raleigh, N. C. 1899.

**A Treatise on Crystallography.** By W. J. Lewis, M.A. Cambridge: At the University Press. 1899. xii+612 pp. Price, 14 shillings net.

**The Urine; and Clinical Chemistry of the Gastric Contents, the Common Poisons, and Milk.** By J. W. Holland, M.D. Sixth Edition, Revised and Enlarged. Philadelphia: P. Blakiston's Son & Co. 1899. vii+124 pp. Price, \$1.00.

**Index to the Literature of Zirconium.** By A. C. Langmuir and Charles Baskerville. City of Washington: Published by the Smithsonian Institution. 1899. 8vo. 29 pp.



**The Chemistry of Essential Oils and Artificial Perfumes.** By Ernest J. Parry. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1899. viii+411 pp. Price, \$5.00.

**A System of Instruction in Qualitative Chemical Analysis.** By Arthur H. Elliott and George A. Ferguson. Third Edition. 1899. Published by the Authors. 115-119 W. 68th St., N. Y. City. 155 pp. Price, \$1.50.

**Traité de la Fabrication des Liqueurs et de la Distillation des Alcools.** Par P. Duplais, aîné. Septième édition, entièrement refendue par Marcel Arpin et Ernest Portier. Tome Premier—Les Alcools. 613 pp. 8 fr. Tome Second. Les Liqueurs. 606 pp. 10 fr. 1900. Paris: Gauthier-Villars. Quai des Grands-Augustins, 55.

**The Cost of Living as Modified by Sanitary Science.** By Ellen H. Richards. New York: John Wiley & Sons. 1899. 121 pp.

**Beginselen der Scheikunde.** Door Dr. M. C. Schuyter. Antwerpen: Jos. Ishoven, Van Straelenstraat, 8. 1899. 109 pp. Price, \$1.50.

**Agricultural Experiment Station of the University of Minnesota.** Bulletin No. 63.—Miscellaneous Analyses, Composition of Tomatoes, Proteids of Wheat Flour. 50 pp. Bulletin No. 65.—Soil Investigation. 84 pp. 1899. St. Anthony Park, Minn.

**The North Carolina Agricultural Experiment Station, Twenty-second Annual Report; Bulletin No. 152-163.** Contents.—Reports of officials; poultry notes; vinegar adulteration; the adulteration of coffee and tea; baking powders; the adulteration of flour; mineraline; the fertilizer control for 1898; horticultural experiments during 1896; digestive experiments; drinking water; farming in North Carolina; rational stock feeding; the flora of North Carolina; preservatives in canned foods; butter; poultry experiments; field and forage experiments; feeding experiments and milk records. lii+462 pp. Raleigh, N. C.

**Lexikon der Kohlenstoff-Verbindungen.** Von M. M. Richter. Zweite Auflage der "Tabellen der Kohlenstoff-Verbindungen nach deren empirischer Zusammensetzung geordnet." Thirty parts. 2000 pp. Price, M. 1.80, per part.

**Petroleum Series—Bulletin No. 3.** The School of Mines, University of Wyoming, Laramie, Wyoming. 32 pp.

**Water and Water Supplies.** By John C. Thresh. Second revised edition. Philadelphia: P. Blakiston's Son & Co. 1900. xv+438 pp. Price, \$2.00.

**Baking Powders.** A treatise on the character, methods for the determination of the values, etc., with special reference to recent improvements in phosphate powders. By Charles A. Catlin. Published by the Rumford Chemical Works, Providence, R. I. 1899. 44 pp.

**Water and Water Supplies.** By John C. Thresh. Second revised edition. Philadelphia: P. Blakiston's Son & Co. 1900. xv+438 pp. Price, \$2.00.



**Annuaire pour l'An 1900**, publié par le Bureau des Longitudes. Avec des Notices scientifiques. 628 pp. **Les Machines Génératrices de Courants Électriques**. Par M. A. Cornu. 89 pp. **Les nouveaux Gaz de l'Atmosphère**. Par M. G. Lippmann. 15 pp. **Les Travaux au Mont Blanc en 1899**. Par M. J. Janssen. **Sur l'Application de l'Aéronautique**. Par M. J. Janssen. 2 pp. **Discours prononcés à l'Inauguration de la Statue de Félix Tisserand**. 19 pp. **Liste des Membres qui Composent le Bureau des Longitudes**. 37 pp. Paris: Gauthier-Villars, quai des Grands-Augustins, 55. In one volume. Price, 1 fr. 50 c.

**The Kinetic Theory of Gases**. Elementary treatise with mathematical appendices. By Dr. Oskar Emil Meyer. Translated from the second revised edition by Robert E. Baynes. New York: Longmans, Green & Co. 1899. xvi + 472 pp. \$4.00.

**Elementary Chemistry for High Schools and Academies**. By Albert L. Arey, C. E. New York: The Macmillan Co. 1899. xi + 271 pp. Price, 90 cents.

**Introduction to Physical Chemistry**. By James S. Walker, D.Sc., Ph.D. London & New York: The Macmillan Co. 1899. x + 335 pp. Price, \$2.50.

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**Commercial Feeding Stuffs in the Connecticut Market**. Connecticut

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Victor von Richter's Organic Chemistry or Chemistry of the Carbon Compounds. Edited by Prof. R. Anschütz (assisted by Dr. G. Schroeter). Authorized translation by Edgar F. Smith, Professor of Chemistry, University of Pennsylvania. Third American, from the Eighth German Edition. Volume II.—Carbocyclic and Heterocyclic Series. Philadelphia: P. Blakiston's Son & Co. 1900. xvi + 671 pp. Price, \$3.00.

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Volumetric Analysis. Specially adapted to the requirements of students entering for the advanced practical chemistry examinations of the science and art department; also the intermediate science and preliminary scientific examinations of the University of London. By John B. Coppock, F.C.S., Inter. B.Sc. (Lond.). London: Whittaker & Co.; New York: The Macmillan Co. 1899. 92 pp. Price, 50 cents.

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### ERRATUM.

In the number for February, 1900, p. 139 line 10, for

“[(CH<sub>3</sub>),NH],TeCl<sub>4</sub>,” read “[(CH<sub>3</sub>),NH] TeCl<sub>4</sub>.”

# THE JOURNAL

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### NOTES ON SELENIUM AND TELLURIUM.

BY EDWARD KELLER.

Received March 26, 1900.

IN a paper under the above title,<sup>1</sup> published some years ago, I pointed out the difference of behavior of selenium and tellurium, in the dioxide state, towards sulphur dioxide and ferrous sulphate in solutions of hydrochloric acid of various strength. The experiments were conducted under definite conditions, as stated in my original paper, the quantities of the two elements being in every case 0.1 gram each, the quantity of the solution 100 cc., and the acidity varying from 0.5 to 100 per cent., the pure hydrochloric acid meaning the aqueous product of 1.175 sp. gr. Based on quantitative determinations of the two elements precipitated by sulphur dioxide in the cold, and other conditions as already stated, the conclusions reached, were as follows: Selenium is most readily precipitated by sulphur dioxide in strong hydrochloric acid. This precipitation continues to be complete until an acidity of 25 per cent. is reached, the solution being allowed to stand about twenty hours. The precipitation, within that time, becomes nil at an acidity of approximately 3 per cent. The precipitation of tellurium in strong hydrochloric

<sup>1</sup> This Journal, 19, 771.

acid is nil. It begins with an acidity of about 80 per cent. (the time of standing as above), becomes complete at about 60 per cent., and continues to be so until the acidity is reduced to about 10 per cent.

On page 774 of the paper cited is found the following remark : " From the above facts we learn that even with sulphur dioxide in a hydrochloric acid solution of over 80 per cent. acid a separation is possible" (meaning a separation of selenium and tellurium).

#### A NEW METHOD OF QUANTITATIVE SEPARATION OF SELENIUM AND TELLURIUM.

That selenium is more readily precipitated by sulphur dioxide than tellurium has long been known and the principle has been practically applied, but, it seems, never to quantitative analysis. Since the publication of my paper, above referred to, I have had occasion in numerous instances to determine the two elements in copper analysis, and I have in all cases applied this hydrochloric acid-sulphur dioxide method. When working with a Gooch filter and a suction pump (filter-paper, of course, cannot be used) this separation is a rapid and simple one. My mode of operation is as follows : 100 grams of copper with from 2 to 4 grams of ferrous sulphate, are dissolved in 400 cc. nitric acid (sp. gr. 1.42) and the nitrous fumes expelled. This solution, after diluting and cooling, is made sufficiently ammoniacal to dissolve all the copper. After boiling and settling, the ferric hydroxide containing the selenium and tellurium is gathered on a filter. It must be freed from copper by washing with ammoniacal water, redissolving in acid, and reprecipitation with ammonia (repeatedly if necessary). This ferric hydroxide is then brought into dilute hydrochloric acid solution (not more acid being used than is necessary to dissolve the precipitate), and hydrogen sulphide passed through the cold liquid until saturation. The solution must be cold to retain the selenium sulphide in soluble form in sodium sulphide, and copper must be absent to guard against insoluble cupric selenide. The sulphides are filtered and washed and digested with a solution of sodium sulphide, which latter takes up the sulphides of selenium and tellurium. The solution, after filtering, is acidified with



**DETERMINATION OF SELENIUM AND TELLURIUM BY PRECIPITATION WITH  
SULPHUR DIOXIDE IN HYDROCHLORIC ACID.**

Selenium.		Tellurium.	
Weighed in.	Found.	Weighed in.	Found.
Gram.	Gram.	Gram.	Gram.
0.1000	0.0983	0.1000	0.0998
0.1000	0.1000	0.1000	0.0986
0.1000	0.1006	0.1000	0.1010
0.1000	0.0994	0.1000	....
0.1000	0.1002	0.1000	0.0993
0.1000	0.1010	0.1000	0.1013
<hr/>		<hr/>	
Av'r'ge 0.1000	0.0999	0.1000	0.1000

The selenium in every case proved to be free of tellurium by its complete solubility in potassium cyanide. Nor could selenium be detected in the filtrates with ferrous sulphate by either increasing or decreasing the strength of the acid. In short, the separation is complete.

In a paper by Mr. Victor Lenher<sup>1</sup> are to be found the following remarks: "When sulphur dioxide is brought into contact with such a strong solution, selenium should be precipitated free from tellurium according to Keller. When sulphur dioxide was introduced into this solution a red precipitate formed, showing selenium just precipitated. It appeared to darken, however, when the liquid was saturated. On boiling, the precipitate agglomerated into a mass which much resembled selenium, but on separating it by means of potassium cyanide it was found to consist of 3.2 grams of selenium and 28.3 grams of tellurium. This seems to indicate that tellurium and selenium cannot be perfectly separated by sulphur dioxide in strong hydrochloric acid solution."

Mr. Lenher worked with 5 pounds of tellurous and selenous material. He does not mention the quantity of acid he used. His conditions were, therefore, probably radically different from those as given in my own experiments.

As I could not doubt my own results of often repeated tests, nor Mr. Lenher's assertions, I inferred that the difference in the conclusions arrived at must be due to the difference in the relative masses of tellurium and acid present in the experiments, and I corroborated this by a few simple tests: The oxides of 0.1 gram of selenium and 5 grams of tellurium were dissolved in

<sup>1</sup> "Preparation of Metallic Tellurium," This Journal, 21, 347.

100 cc. of 90 per cent. hydrochloric acid, and the solution saturated with sulphur dioxide. The precipitate, after standing about twenty hours, contained all of the selenium with 2.1 grams of tellurium. In the subsequent tests the acid of the same strength was increased each time by 50 cc., the quantities of selenium and tellurium remaining constant. The quantity of tellurium decreased in each successive precipitation, and became nil when the quantity of acid reached 450 cc. It follows, therefore, that to obtain a perfect separation of selenium and tellurium in strong hydrochloric acid solution by means of sulphur dioxide, the quantity of acid must be about 100 times that of the tellurium.

Numerous chemists have pointed out the error made in determining tellurium in its metallic state, it being due to slight oxidation. Mr. F. H. D. Crane<sup>1</sup> found this error to be from 0.3–0.6 per cent. over the correct result, when no precautions were taken. Criticism for using this method in industrial practice seems to me entirely unjustified. Although accuracy is always essential, the practical chemist must be able to discriminate between accuracy and pedantry. For example: Our copper rarely contains as much as 0.01 per cent. of tellurium, and we should find, according to Mr. Crane, when using 100 grams of copper, from 0.01003 to 0.01006 instead of 0.01 gram of the element, a difference absolutely beyond detection and of no importance whatsoever in ordinary work. In fact, the chemist would find, in practice, that with more scientific methods  $\pm 3$  or 6 per cent. would often be far from covering the differences between his own duplicates, or those of other equally conscientious workers. In substantiation of this I need only refer to the determination of small percentages of precious metals,<sup>2</sup> upon which large commercial interests depend. With silver, which occurs in larger quantity than tellurium, determinations often differ  $\pm 3$  to 5 per cent. from the mean. With gold, occurring in smaller quantities, these variations rise as high as  $\pm 25$  per cent.

BALTIMORE, March, 1900.

<sup>1</sup> "A Contribution to the Knowledge of Tellurium," Dissertation, Johns Hopkins University, 1898.

<sup>2</sup> "Assays of Copper and Copper Matte," *Trans. A. I. M. E.*, 25, 250.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, U. S. DEPARTMENT  
OF AGRICULTURE, No. 37.]

## THE ESTIMATION OF ALUMINA AND FERRIC OXIDE IN NATURAL PHOSPHATES.<sup>1</sup>

BY F. P. VEITCH.

Received March 22, 1900.

THE search for an accurate and rapid method for the determination of alumina and iron oxide in the presence of phosphoric acid has occupied the attention of analysts for years, and many methods have been proposed for this difficult operation. It may be said generally that even those methods that have stood the tests of extended use have not escaped severe criticism; they are only accurate within narrow and rigidly defined limits or they are tedious and time-consuming.

Aside from its interest from the scientific point of view, this subject is of importance in its technical and commercial aspects. The value of raw mineral phosphates, which, in the United States alone, for the year 1893, Wiley estimates at \$4,157,070,<sup>2</sup> is determined largely by their content of alumina and iron.

In phosphatic slags the estimation of these oxides is more difficult, though possibly not so important.

### SOURCES OF ERROR IN THE OLDER METHODS.

The Glaser alcohol, the acetate with its various modifications, and the caustic alkali, methods as carried out by Lasne, Lichtschlag, and by Gladding, have all been severely criticized and the following sources of error pointed out by various observers:<sup>3</sup>

1. In the Glaser alcohol method, the precipitation of manganese with the iron and aluminum phosphates, and solubility of the phosphates in the wash-water. Probably the manganese can be eliminated by a second precipitation in the presence of a large amount of ammonium chloride. Possibly the presence of a large amount of ammonium sulphate may also effect the accuracy of this method, in those cases where the excess of ammonia is com-

<sup>1</sup> Abstract of Thesis presented to the Faculty of the Graduate School of Columbian University and accepted for the degree of Master of Science, June, 1898. Presented to the American Chemical Society, Boston Meeting, 1898.

<sup>2</sup> U. S. Department of Agriculture, Yearbook, 1894.

<sup>3</sup> Wiley's "Principles and Practice of Agricultural Analysis," Vol. II, pp. 24, *et seq.*



pletely removed by boiling. Aluminum phosphate is noticeably soluble in a strong sulphate solution, which is neutral or faintly acid from  $\text{SO}_3$ .

2. In the acetate method and its variations, the precipitation of the lime with the iron and aluminum phosphates, solubility of aluminum phosphate in cold acetate solutions, solubility and dissociation of iron and aluminum phosphates in water,<sup>1</sup> also when the phosphates are fused with sodium carbonate, and the iron determined by precipitation with ammonia, the contamination of the iron with calcium phosphate, which is not always entirely decomposed by fusion. Of these the most serious sources of error are the first and the last mentioned.

3. In the caustic alkali methods, there is danger of some of the aluminum being held by the voluminous precipitate produced by the alkali; there is also danger of alumina being precipitated if much carbon dioxide is absorbed; Lasne and Lichtschlag have shown that while the method is long it gives accurate results if properly conducted. Blaltner and Brasseur<sup>2</sup> have recently investigated the more important methods and conclude:

“The acetate method should be discontinued; figures for alumina are nearly always too low.”

Glaser method (alcohol) gives accurate results in the absence of manganese.

The caustic soda method, as carried out by Lasne, gives exact results. Gruber's and Gladding's methods are condemned.

In view of these many sources of error in the conventional methods, considerable time has been devoted to the study of a method that, it is hoped, is free from most of the above-mentioned objections. It is an adaptation, so far as possible, of the good points of the present best methods. From the precipitating reagent, it may be designated

#### THE THIOSULPHATE METHOD.

The use of a soluble thiosulphate for the separation of alumina from iron and aluminum from several other metals seems to be due to G. Chancel.<sup>3</sup> Later it was used by Stead and by Car-

<sup>1</sup> *Chem. Ztg.* (1897), p. 264; also Fresenius.

<sup>2</sup> *Bull. Soc. Chim.* [3], 17, 18, No. 15.

<sup>3</sup> *Compt. rend.*, 46, 98.

not;<sup>1</sup> by the latter for the separation of aluminum as phosphate, in the presence of ammonium acetate, from iron. Lasne<sup>2</sup> also uses it to precipitate aluminum phosphate in the presence of ammonium acetate, after removing iron, lime, etc., with caustic soda.

From the available literature on the subject it seems that a method based on the separation of aluminum phosphate from iron and lime by a thiosulphate and ammonium chloride alone, may be used for the determination of aluminum in the common natural phosphates.

Considerable work has been done with the method to gain familiarity with it and to test its applicability under various conditions and in the presence of various salts. For this work a chemically pure aluminum sulphate was prepared in which alumina has been carefully determined. This salt was used for all the tests.

The preliminary work under varying conditions, following the method as laid down by Chancel and by Carnot, did not always give concordant results, frequently being low. A brief study suggested the cause of this, and the addition of a considerable quantity of ammonium chloride led to much better results. The principle upon which the method is based is the insolubility of aluminum phosphate in a strong neutral solution of ammonium chloride. The thiosulphate has nothing to do with the precipitation, except that it is an exact method of obtaining the desired neutrality. Thomson<sup>3</sup> has devised a method in which he makes use of this principle, neutralizing with ammonia, using a delicate indicator to determine neutrality.

*Study of the Proposed Method.*—One of the first problems presented in the study of any method for the determination of alumina as phosphate is the composition of the ignited phosphate. Observers do not agree as to this. While all agree that the normal phosphate is only obtained in the presence of an excess of phosphoric acid, they do not agree that it is always obtained, even under these conditions.<sup>4</sup>

<sup>1</sup> Blair's "Chemical Analysis of Iron," second edition, 185, 186.

<sup>2</sup> *Bull. Soc. Chim.*, 15, 118.

<sup>3</sup> *J. Soc. Chem. Ind.*, 15, 868.

<sup>4</sup> *Chem. Ztg.* (1897), pp. 264, and 21, 116; Wiley's "Principles and Practice of Agricultural Analysis," Vol. II, p. 24; Blair's "Chemical Analysis of Iron," second edition, 185; S. C. Agr. Expt. Sta., Bull. No. 2.

*Wash Solutions.*—It seems that the solution of this problem can only be obtained by a study of the solutions used in washing the precipitate. Besides waters of all temperatures, solutions of various salts, such as 5 per cent. ammonium nitrate, ammonium chloride, 1 per cent. ammonium nitrate plus 0.02 per cent. ammonium phosphate, and dilute ammonium acetate, have been proposed and used by many investigators. These various washes possibly account for the variations from the normal, so frequently noted. In the brief mention of some of the observed sources of error in the conventional methods it was shown, by numerous authorities, that the recently precipitated phosphates of iron and aluminum, when freed from adhering salts, are slightly soluble, or rather are dissociated, in water of any temperature. Those who have apparently used water successfully as a wash probably did not wash enough, only three or four times, to remove the adhering salts. Cold ammonium or sodium acetate also slowly dissolves aluminum phosphate.

The effects of the following wash liquors have been studied :

Water at from 60° to 70° C.

5 per cent. ammonium nitrate at from 60° to 70° C.

1 " " " " " " 60° " 70° C.

5 " " " " and 0.02 per cent. ammonium phosphate at from 60° to 70° C.

*Method of Study.*—Various quantities of the C. P. aluminum sulphate were placed in a 12-ounce beaker with a solution of 2 grams of ammonium phosphate, the resulting precipitate dissolved in hydrochloric acid, and 25 cc. of a 50 per cent. solution of ammonium chloride added. The solution was then made alkaline with ammonia and the precipitate just dissolved with hydrochloric acid, noting approximately the number of cubic centimeters required after the solution had become acid ; the solution was then diluted to about 250 cc., and for each cubic centimeter of hydrochloric acid added to the acid solution 5 cc. of a 50 per cent. solution of ammonium thiosulphate were added dropwise, the beaker covered with a watch-glass, the solution boiled half an hour, filtered, washed, dried, and ignited to constant weight.

The results are given in Table I. All results in the work have been corrected by blank determinations on the reagents

TABLE I.

	Wash solution.	Times.	Washings.		Al <sub>2</sub> O <sub>3</sub> . Theory. Mgs.	Al <sub>2</sub> O <sub>3</sub> . Found. Mgs.	Error. Mgs.
			Volume.	cc.			
Water 60° to 70° C.....		40		500	159.7	155.9	—3.8
“ 60° “ 70° C.....		20		250	39.9	38.2	—1.7
5 per cent. ammonium nitrate, 60° to 70° C.....		20		250	39.9	39.8	—0.1
5 “ “ 60° to 70° C.....		20		250	79.8	79.6	—0.2
5 “ “ 60° to 70° C.....		20		250	79.8	80.1	—0.3
5 “ “ 60° to 70° C.....		50		650	79.8	78.9	—0.9
5 “ “ 60° to 70° C.....		50		650	79.8	79.3	—0.5
I “ “ 60° to 70° C.....		20		250	39.9	39.3	—0.6
I “ “ 60° to 70° C.....		20		250	79.8	79.2	—0.6
I “ “ 60° to 70° C.....		20		250	79.8	78.8	—1.0
I “ “ 60° to 70° C.....		20		250	79.8	77.4	—2.1
I “ “ 60° to 70° C.....		20		250	79.8	79.2	—0.6
I “ “ 60° to 70° C.....		20		250	79.8	79.2	—0.6
5 “ (NH <sub>4</sub> ) <sub>2</sub> NO <sub>3</sub> +0.02 per cent. (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> ..		20		250	79.8	80.9	—1.1
5 “ “ “ “ “		20		250	79.8	80.2	—0.4

employed ; and all precipitations were made in the presence of an excess of phosphoric acid.

An examination of the table shows that, of the wash solutions, 5 per cent. ammonium nitrate washing twenty times gives practically theoretical results. As many as 50 washings with this solution give results slightly low but still good. The other solutions were rejected as they showed a decided solvent effect, except the ammonium nitrates plus ammonium phosphate, upon prolonged washing. Twenty washings were required to free the precipitate from chlorides, sulfates, and ammonium phosphate. In all succeeding work 5 per cent. ammonium nitrate was used, washing twenty times unless otherwise stated. Long heating with the blast, ten to twenty minutes, was required to reduce to constant weight.

*Composition of the Ignited Aluminum Phosphate.*—The phosphoric acid, in the aluminum phosphate washed twenty times with 5 per cent. ammonium nitrate, was carefully determined by precipitation with molybdate solution, washing the precipitate of ammonium phosphomolybdate with dilute nitric acid, and washing the final precipitate free of chlorides.

	Theory. P <sub>2</sub> O <sub>5</sub> . Mgs.	Found. P <sub>2</sub> O <sub>5</sub> . Mgs.
a .....	58.2	58.8
b .....	...	58.7
c .....	...	58.8
		<hr/>
		Average, 58.8

The salt obtained under the above-mentioned conditions seems to be the normal phosphate, AlPO<sub>4</sub>.

THE EFFECT OF THE PRESENCE OF SALTS OF SOME OTHER METALS.

*Effect of Iron Salts.*—Five grams of ammonium ferric alum dissolved in water, 2 grams of ammonium phosphate added, and treated as for aluminum phosphate, washing twenty times with ammonium nitrate, gave :

	Calculated as alumina. Mgs.
a.....	4.5
b.....	0.0
c.....	1.3
d.....	0.0
Precipitated while slightly warm.	

Another series precipitated twice gave :

	Calculated as alumina. Mg.
<i>a</i> .....	0.4
<i>b</i> .....	0.0
<i>c</i> .....	0.0
<i>d</i> .....	0.0

Solutions containing aluminum sulphate, ammonium phosphate, and 5 grams of ammonium ferric alum precipitated once with ammonium thiosulphate, gave :

	Theory. Mgs.	Al <sub>2</sub> O <sub>3</sub> found. Mgs.
<i>a</i> .....	78.9	86.4
<i>b</i> .....	23.9	28.2

Both contained iron.

Similar solutions precipitated twice with sodium thiosulphate, gave :

	Theory. Mgs.	Al <sub>2</sub> O <sub>3</sub> found. Mgs.
<i>a</i> .....	39.9	39.4
<i>b</i> .....	39.9	40.8

These precipitates contained no iron.

Therefore, in the presence of large quantities of ferric iron, two precipitations only are necessary to separate the iron.

*Effect of Calcium Salts.*—Two grams of calcium phosphate, precipitated once, gave :

*a*, Nothing.

*b*, “

Aluminum phosphate plus 2 grams calcium phosphate, precipitated once, gave :

	Theory. Mgs.	Al <sub>2</sub> O <sub>3</sub> found. Mgs.
<i>a</i> .....	79.8	80.1
<i>b</i> .....	79.8	80.8
<i>c</i> .....	79.8	81.0
<i>d</i> .....	23.9	24.3
<i>e</i> .....	79.8	80.2
<i>f</i> .....	79.8	79.3

*a*, *b*, *c*, and *d* were washed twenty times with 5 per cent. ammonium nitrate; *e* and *f* were washed fifty times.

The error produced by the presence of calcium salts alone is

not so great as that produced by iron salts. In this case it seems probable that the error is produced by the well-known property of the aluminum precipitates of carrying down other salts mechanically. Two precipitations separate completely aluminum phosphate from very large quantities of iron and of lime, as is shown by the following data :

$\text{Al}_2(\text{SO}_4)_3$ Gram.	$\text{Ca}_3(\text{PO}_4)_2$ Gram.	$\text{NH}_4\text{Fe}(\text{SO}_4)_2$ Gram.	$\text{Al}_2\text{O}_3$ Theory. Mgs.	$\text{Al}_2\text{O}_3$ Recovered. Mgs.
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	39.9	39.6
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	19.9	18.8
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	19.9	18.8
$\frac{1}{2}$	2	1 iron	39.9	39.7
$\frac{1}{2}$	2	1 "	39.9	39.9

From the foregoing results the conclusion seems warranted that aluminum phosphate can be quantitatively separated by a soluble thiosulphate and ammonium chloride from a hydrochloric acid solution of iron, alumina, and lime phosphates containing only a small amount of sulphates. The statement of many observers, that theoretical results on aluminum phosphates can only be obtained in the presence of an excess of phosphoric acid, has been confirmed by my own work. The error produced by precipitating a second time without adding phosphoric acid amounted in some cases to 2 mgs. alumina. •

*The Effect of Magnesium, Sodium, and Potassium Salts.*—Three solutions containing in 50 cc. the following :

	A. Gram.	B. Gram.	C. Gram.
Calcium phosphate.....	0.8000	0.7000	.....
Calcium chloride.....	.....	.....	0.250
Magnesium chloride.....	0.0200	0.0100	0.0250
Potassium chloride.....	0.0100	.....	.....
Sodium chloride.....	.....	0.0100	.....
Iron .....	0.0185	0.0421	0.0125
Sodium hydrogen phosphate .	.....	.....	2.0000
Aluminum sulphate.....	0.3504	0.1504	0.1000

gave

	A.		B.		C.	
	Theory. Mgs.	Found. Mgs.	Theory. Mgs.	Found. Mgs.	Theory. Mgs.	Found. Mgs.
Alumina ....	56.0	54.5	24.0	24.2	16.0	15.8
	56.0	56.3	24.0	23.9	16.0	15.8

The above-named salts therefore exert no disturbing influence on the accuracy of the final results.

*The Effect of Silica.*—It is stated by Carnot<sup>1</sup> that “In the presence of silica the precipitate of aluminum phosphate contains a little silica.” I have tried to remove this silica by two precipitations but have failed, the plus error equivalent to  $\text{Al}_2\text{O}_3$  being,

	Mgs.
<i>a</i> .....	1.2
<i>b</i> .....	0.6
<i>c</i> .....	3.3
<i>d</i> .....	2.5

In order to secure correct results, therefore, the silica must be removed from the mixture before the separation of the aluminum phosphate.

*The Effect of Sulphates.*—Removal of silica being a necessary operation it was determined to make the separation by the well-known method based on the insolubility of silica in sulphuric acid. This method, worked out very carefully by Drown,<sup>2</sup> is a very rapid and accurate process, which is used almost exclusively in the determination of silica in pig-iron. Essentially the same method has been worked out and used by others for the determination of silica in furnace products.

While the separation of silica by this method is all that can be desired it was found to be impossible to completely precipitate the aluminum phosphate with a thiosulphate in the filtrate.

From solutions containing various quantities of the sulphates, phosphates, and chlorides of iron, aluminum, and lime, the following results were obtained :

Experiment.	$\text{H}_2\text{SO}_4$ present. Grams.		Alumina.	
			Theory. Mgs.	Found. Mgs.
2	0.100	1 precipitation	39.9	39.8
11	0.20	1 “	79.8	79.6
12	0.20	1 “	....	80.1
19	0.20	1 “	....	80.1
20	0.20	1 “	....	80.8
20a	0.10	1 “	23.9	24.2
33a	1.250	2 “	39.9	39.6
34a	1.250	2 “	....	40.7

<sup>1</sup> Blair's “Chemical Analysis of Iron,” p. 188.

<sup>2</sup> *J. Inst. Min. Eng.*, 7, 346.



Experiment.	$H_2SO_4$ present. Grams.			Alumina.	
				Theory. Mgs.	Found. Mgs.
50	2.800	2	"	....	38.7
35a	7.500	2	"	19.9	16.8
36a	7.500	2	"	....	18.7
39c	7.500	2	"	39.9	37.9
39d	7.500	2	"	....	37.8
38a	36.000	1	"	31.9	17.2

The presence of more than 1.25 grams of sulphuric acid prevents the complete precipitation of aluminum phosphate, while 2.75 grams give a decided error. The presence of ammonium acetate did not give any better result; see result marked "Experiment 50."

*The Effect of Fluorine.*—The presence of a fluoride in a solution from which it is attempted to separate aluminum by this method is as disastrous to the results as is the presence of sulphates. From solutions containing phosphates, chloride, and small amounts of sulphates of aluminum, iron, magnesia, lime and soda, and fluoride, the results below are obtained :

				Fluorine present. Mgs.	Alumina.	
					Theory. Mgs.	Found. Mgs.
a	2	precipitation		50	39.9	28.4
b	2	"		50	....	27.4
c	2	"		50	19.9	8.9
d	1	"		250	36.9	31.6
e	2	"		250	....	28.5
f	2	"	1st 10 cc. $CH_3COONa$		....	25.3
g	2	"	" " "	"	19.9	14.9
h	2	"	" " "	"	39.9	31.0
i	2	"	" " "	"	19.9	16.6

In none of the current methods is the presence of fluorine mentioned as a disturbing factor. Several determinations by the acetate method, both single and double precipitation in the presence of dissolved calcium fluoride, showed that it has no effect.

Experiment.	$CaF_2$ present. Mgs.	Alumina.	
		Theory. Mgs.	Found. Mgs.
60a	250	39.9	40.9
60b	250	...	38.1
60c	125	19.9	19.4
60d	125	...	19.8

*The Effect of Manganese, with solutions containing :*

	Gram.
Aluminum sulphate .....	0.25
Calcium phosphate .....	0.5
Ammonium ferrous alum .....	0.25
Magnesium chloride.....	0.10
Manganese chloride .....	0.10

The following data were obtained :

Experiment.	Alumina.	
	Theory. Mgs.	Found. Mgs.
64a	39.9	40.5
64b	....	40.3

The work so far done shows that alumina can be quantitatively separated as phosphate from a hydrochloric acid solution containing aluminum, iron, manganese, lime, magnesium, sodium, and potassium, when only small quantities of sulphate are present, and that the presence of silica in the solution produces a plus error too large to be neglected, and that the presence of large quantities of sulphates or the presence of fluorides prevents the complete precipitation of aluminum phosphate. Therefore, to obtain accurate results, silica and fluorine must be removed while sulphates, not more than the equivalent of 1.25 grams of sulphuric acid, may be present.

The following method for alumina in phosphates is based upon the results of these experiments: Treat 1 gram of substance in a platinum dish with from 5 to 10 cc. hydrofluoric acid, let stand in the cold from two to three hours, heat on the water-bath to complete dryness, add 2 cc. concentrated sulphuric acid, running well around the sides, and heat at a low temperature until the substance no longer flows in the dish. By this process fluorine is completely expelled. Cool and add from 10 to 20 cc. concentrated hydrochloric acid, and warm a few minutes to soften the mass; transfer to a small beaker, and boil until all aluminum compounds are surely dissolved (fifteen to thirty minutes); filter from undissolved residue, if any, washing the filter thoroughly, add 50 cc. 25 per cent. ammonium chloride solution and ammonia until alkaline, then hydrochloric acid until the precipitate just dissolves. Cool, dilute to about 250 cc., and add 50 per

cent. sodium thiosulphate solution, drop by drop, until the solution is colorless, adding in all 20 cc.; cover with a watch-glass, boil half an hour, filter, wash back into the same beaker, and dissolve in boiling hydrochloric acid; reprecipitate exactly as before, after adding 2 cc. of a 10 per cent. ammonium phosphate solution. Wash twenty times with 5 per cent. ammonium nitrate solution, and ignite to constant weight. For the second precipitation ammonium thiosulphate may also be used but it is not strictly necessary.

According to the above method from solutions containing :

	Mgs.
Aluminum sulphate.....	250
Calcium phosphate.....	500
Ammonium ferrous alum.....	250
Silica .....	100
Calcium fluoride .....	100
Manganese chloride .....	100
Magnesium chloride.....	100

These results recorded below were obtained :

Experiment.	Alumina.	
	Theory. Mgs.	Found. Mgs.
63a	39.9	40.0
63b	....	39.5
63c	....	40.1
63d (contained fluorine)	....	37.8
63e	19.9	19.6
63f	....	20.3
65a	39.9	39.5
65b	....	39.9
66a No. 1 ground S. C. rock	17.0 by acetate method	18.4
66b	....	17.8
67a " 4 " Florida	19.4 " " "	16.3
67b	....	14.3

Move the decimal one place to the left to express percentages.

The phosphoric acid was determined in the aluminum phosphate obtained in Experiment No. 63.

	Theory. Mgs.	Pound. Mgs.
a .....	58.2	58.0
b .....	...	57.6
c .....	...	57.2

Here, also, the phosphate seems to be the normal,  $\text{AlPO}_4$ , although it was separated in the presence of all substances likely to be found in a natural phosphate, with the exception of silica and fluorine.

The greatest difficulty to be overcome in the execution of this method is the error produced by the presence of fluorine; hence it is necessary to heat the substance for a long time with sulphuric acid to insure the complete removal of fluorine before beginning the separation of the aluminum phosphate.

An attempt to overcome this source of error by adding an alkaline acetate before boiling with thiosulphate gave no better result. In one experiment, however, in which the acetate was added after the boiling, and ten minutes before filtering, all the aluminum phosphate was removed.

The determination of ferric oxide was made as follows: Dissolve 1 gram of substance in 20 cc. sulphuric acid, dilute, filter, washing the filter thoroughly, and if any organic matter is present add a little potassium chlorate and boil until chlorine is expelled. Reduce with zinc, filter, and titrate at once with potassium permanganate solution, 1 cc. of which equals 0.0025 gram ferric oxide.

From solutions used in Experiment 63 I obtained:

	Ferric oxide.	
	Theory. Mgs.	Found. Mgs.
<i>a</i> .....	51.8	52.5
<i>b</i> .....	....	52.2
<i>c</i> .....	....	52.2
<i>d</i> .....	....	52.2
<i>e</i> .....	....	51.7
<i>f</i> .....	....	51.4
No. 1 ground S. C. rock..	30.6 by acetate method	29.4
	....	29.3
" 4 " Florida "	.. 14.5	15.4
	....	15.1

I desire to express my thanks to Prof. H. W. Wiley, who assigned this subject for my thesis, and for the valuable assistance given me during the conduct of the work.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESLEYAN UNIVERSITY.]

## THE DISTILLATION OF AMMONIA IN THE DETERMINATION OF NITROGEN.

BY FRANCIS GANO BENEDICT.

Received March 27, 1900.

THE distillation of ammonia in the moist combustion process for determining nitrogen involves the separation of the gaseous ammonia from the alkaline liquid in the distilling flask and the transportation of the gas through a tube into the receiver. While the disengagement of ammonia from a strongly alkaline liquid is readily accomplished by the aid of heat the complete removal of ammonia from the condenser tube is only affected by prolonged boiling to wash the ammonium hydroxide formed out of the tube or by conducting live steam through the tube to vaporize the ammonia which is then driven by the water vapor into the receiver.

The first method is that employed in most laboratories in this country and is designated the "official" method. The second method is that employed in many German laboratories and is here designated the German method.

In the official method the distillation is continued until about 150 cc. of the distillate have been condensed and it is assumed that all the ammonia will have been transferred to the receiver during this operation. The gaseous ammonia coming in contact with the cold water adhering to the inside of the condenser tube dissolves in it forming ammonium hydroxide. The steam generated in the flask condenses in the upper part of the tube and the water formed, slowly runs down, washing out the ammonium hydroxide. It is easily seen that a considerable amount of water would be necessary to insure complete removal of the alkali in this way. Experience has shown that not less than 150 cc. of distillate can safely be relied on to effect this result. This requirement is both expensive and tedious. The operation requires, as a general rule, from forty-five minutes to one hour. Of this time probably not over fifteen to twenty minutes are required to drive all the ammonia out of the liquid, the remaining time being occupied in washing the ammonium hydroxide out of the condenser tube.

According to the German method, the vapors are conducted from the distilling flask through a pipe into the acid, in the receiver with no preliminary cooling, and as a result the contents of the receiver are soon heated to boiling by the latent heat of the steam. Under these conditions, it has been found that after vigorously boiling for twenty minutes all ammonia has been driven out of the alkaline liquid in the distilling flask. Inasmuch as the conditions in this flask are the same in both cases it is only correct to assume that in the official method the ammonia is entirely expelled from the liquid in the same length of time.

Under the conditions existing in the distilling flask by the German method probably no ammonium hydroxide is formed in the condenser tube as the whole system is almost immediately brought to the temperature of steam. Accordingly the gaseous ammonia is carried along mechanically by the water vapor and conducted directly into the receiver.

The great saving in time and gas of this method over the official method is, however, partially offset by the fact that the contents of the receiver at the end of the distillation must be cooled before the titration is made when (as is commonly the case) ammonium hydroxide is used as a standard alkali. Unless the receiver is well cooled, a loss of ammonia is sure to occur.

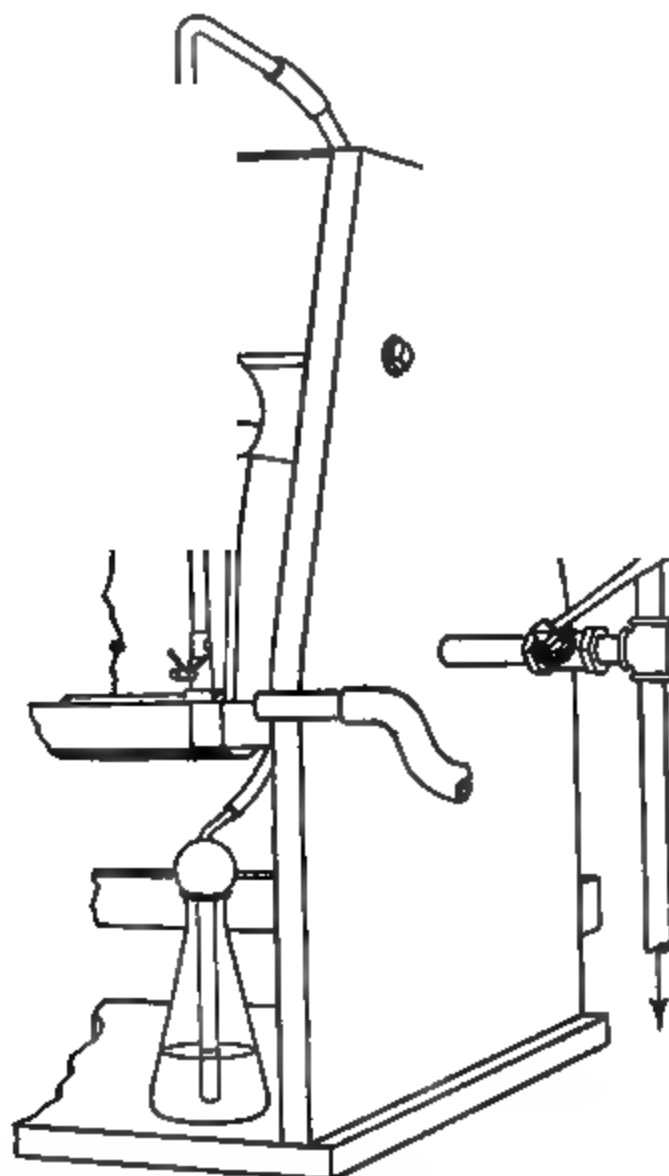
A further objection to the German method lies in the fact that a loss of acid is experienced by the passage of so much steam through the hot liquid in the receiver. This loss should not be neglected in accurate work.

The following modification is, in reality, a combination of the official and the German method, and consists briefly of distilling the liquid into a condenser containing cold water which is allowed to run out a few moments before the end of the distillation that the condenser tubes may become heated. The ammonia in the tubes is then vaporized and driven into the receiver by a current of live steam. By this means the rapid removal of ammonium hydroxide in the condenser tubes is effected without unduly heating the contents of the receiver.

The apparatus which has been in constant use in this laboratory for over a year is shown, in part, in the accompanying figure.

The principal feature is the arrangement of the condenser, a galvanized-iron tank 148 cm. long, 38 cm. deep, and 8 cm. wide.

Ten pieces of block tin pipe 4 mm. internal diameter and 70 cm. long are soldered as usual in the bottom of the tank with ends about 6 cm. long extending through for connection with the receiver and bulb. The upper ends are fastened to one side of



the tank and each is provided with a rubber tube to which a Hopkins' safety distilling bulb is attached.

At one end of the tank and near the bottom a piece of standard half inch pipe is inserted, fitted with a valve or gate which is in turn connected with a T. An overflow is provided near the top of the tank and is connected with the T, the lower arm of which is connected with a sink or drain. The tank which is filled from a water tap at the other end is fastened on a stout frame 35 cm. above the table. The space below is occupied by the receivers and bulb tubes used to prevent back suction of liquid.

<sup>1</sup> This Journal, 18, 227.

With the form of apparatus above described the distillation is carried out as follows: The gas is turned on full and the burners are all lighted.<sup>1</sup> As the liquid in the distilling flask is quite warm from the heat of the dilution of the sulphuric acid and the heat generated by the reaction between the acid and the alkali, the flasks are all vigorously boiling, as a rule, inside of four or five minutes. When all are boiling the time is noted and at the expiration of fifteen minutes the valve is opened, allowing the water to flow out of the condenser. As the water runs out the cold water at the bottom is first withdrawn, the layer of hot water at the top gradually settling and warming the block tin pipes. Just before the layer of hot water begins to flow out the whole condenser tube becomes hot enough to prevent any condensation of water and the live steam blows through the tube into the receiver. This is allowed to continue till the water in the receiver is warmed slightly, the degree of warming being readily determined by occasionally placing the hand on the receiver. As soon as a rise in temperature is perceptible the receiver and bulb are disconnected. This operation requires from four to six minutes after opening the water valve in the apparatus here used. The contents of the flask are therefore vigorously boiling for from nineteen to twenty-two minutes. Repeated tests have shown that all the ammonia is driven off under these conditions. With excessive amounts of ammonia, the boiling operation can be prolonged five minutes before opening the valve. This is seldom necessary, however. Ordinarily, twenty-five to thirty minutes from the lighting of the gas under the flasks to the removal of the receivers suffice to complete the distillation. The titrations can be made immediately.

The length of time necessary to draw off the water in the condenser tank to such a level as to cause live steam to blow through the block tin pipes, is determined by the sizes of the waste pipe and the condenser. With very little experience, it is not difficult to determine how long after boiling the valve should be opened to produce the desired effect at the end of twenty minutes.

The condenser tank here described was not constructed pri-

<sup>1</sup> The use of Jena glass digestion as well as distillation flasks is strongly recommended. With such flasks the full free flame may be employed with impunity. The distillation flasks contain approximately 500 cc. and are about half filled with the alkaline liquid.



marily for this method of distillation. It could undoubtedly be diminished very materially in size with equally satisfactory results.

Obviously the principle is capable of application to numerous forms of condensers. It is only necessary to observe that the flasks are vigorously boiling for at least nineteen or twenty minutes. In a local laboratory the principle has been easily applied to a two-tube condenser constructed out of an old ether can. This apparatus has also given excellent satisfaction for over a year.

MIDDLETOWN, CONNECTICUT.

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## THE GLUTEN CONSTITUENTS OF WHEAT AND FLOUR AND THEIR RELATION TO BREAD-MAKING QUALITIES.

BY H. A. GUESS.

Received March 22, 1900.

**D**URING the last eighteen months the writer has been pursuing some investigations in the chemical factors which determine bread-making qualities of wheats and flours, and the notes here submitted, representing some results of the work, are offered as contributions to the chemical literature of an as yet rather neglected subject.

As aids in the work advantage was taken of published notes by other investigators, acknowledgments being more particularly due to the papers of M. E. Fleurent,<sup>1</sup> and of Mr. G. L. Teller.<sup>2</sup>

The result of considerable preliminary work in the estimation of the proteids of both wheats and flours, and subsequent comparisons with results of milling and baking tests, led the writer to confine his attention more particularly to the determination of the gluten constituents gliadin and glutenin, as being apparently the chief determining factors in bread-making qualities.

In the estimation of the gliadin and glutenin, five nitrogenous bodies were considered as being present in the samples,—gliadin,

<sup>1</sup> "Sur la composition immédiate du gluten des cereals."—*Compt. rend.*, 123, 327.

"Determination of Gluten in Wheat Flour."—Third Congress of Applied Chemistry. Vienna, August, 1898.

<sup>2</sup> "Concerning Wheat and its Mill Products: A report of progress of investigations in the chemistry of wheat."—Arkansas Expt. Station, 1898.

glutenin, edestin, leucosin, and the amides. For the separation of the gliadin, alcohol of 0.90 sp. gr. was used, and after deducting the nitrogen of the amides present, the balance of the nitrogen in the alcohol extract, was calculated as gliadin.<sup>1</sup>

The nitrogen of the amides was determined on a separate sample, by extraction with one per cent. salt solution, precipitating all proteids with phosphotungstic acid, and determination of the amide nitrogen in the filtrate.

The edestin and leucosin were separated from the residue from the alcohol extraction, by extraction with one per cent. salt solution, and the nitrogen remaining in the final residue, calculated as glutenin. By making the 1 per cent. salt solution extraction on the residue from the alcohol extract, any uncertainty from partial solubility of gliadin, or allied proteid bodies, in salt solution, was avoided.<sup>2</sup>

The *modus operandi* of the analysis, was as follows :

a. Five grams of the finely ground wheat meal or flour, placed in a 250 cc. flask, 1 per cent. salt solution added from a pipette, at sufficient pressure to prevent any tendency to clot ; flask filled to the mark, shaken at intervals for one hour, and let settle for two hours ; decanted through a filter, duplicate portions of 100 cc. each of the clear supernatant liquid withdrawn, the proteids precipitated with a few cubic centimeters of 10 per cent. solution of phosphotungstic acid, the precipitate allowed to settle, 50 cc. of the clear filtrate evaporated with sulphuric acid, and the amide nitrogen determined.

b. One gram of sample put in a 500 cc. Kjeldahl flask with 100 cc. alcohol of 0.90 sp. gr., shaken to thoroughly mix, placed on a water-bath, and maintained at a temperature slightly below the boiling-point of the alcohol mixture ; agitated every ten minutes for one hour, allowed to settle for one hour and decanted into a similar flask, being careful to not carry decantation close enough to cause any turbidity to appear in the decanted filtrate ; 25 cc. fresh hot alcohol added, allowed to settle twenty minutes, decanted, and the operation repeated three times. In the extract, the alcohol is distilled off, and the nitro-

<sup>1</sup> *Am. Chem. J.*, 15, 441.

<sup>2</sup> *Ibid.*, 392 *et seq.*

gen in the residue determined, the amide nitrogen ( $a$ ) subtracted, and the balance calculated as gliadin ( $N \times 5.7$ ).

c. To the residue from the alcohol extraction, after cooling, 250 cc. of 1 per cent. salt solution are added; it is allowed to settle for one hour, and decanted through a filter; 250 cc. fresh salt solution are added, shaken at intervals for one hour and allowed to settle for two hours, decanting through the same filter; the filter and contents are added to the residue in the flask, and nitrogen determined and calculated to glutenin.

Following are results of some determinations made in this way on wheats from different elevator points, throughout the Canadian Northwest, giving the locality, the buyer's regular grading mark, the percentages of gliadin and glutenin respectively; the ratio of same, and a composite factor representing this ratio  $\times$  the total percentage of gluten (gliadin and glutenin) present. Also of the same determinations made at regular intervals on the flours produced from these wheats, by one of the largest milling companies in Canada. Analyses of the different 'break' products of the mill were also similarly made, but are not here included.

This ratio of gliadin to glutenin has been used tentatively, as an index of the gluten quality. So far as the writer has been enabled to have this index checked by actual baking tests on the flour produced, it was found that the elastic quality of the gluten was improved in proportion as the ratio of gliadin to glutenin increased, and as yet no limit has been found beyond which further increase of gliadin ratio rendered the gluten inelastic or sticky.

Manifestly, if this ratio of gliadin to glutenin be a true index of the quality of the gluten, the factor of quantity must also be taken account of in estimating the true gluten value of a wheat or flour, the value being the total number of units of gluten present  $\times$  the value per unit. Need was felt, in the work, for a factor to indicate this gluten value, so as to be of use commercially, in grading wheats and flours, and in the lists following this gluten value is in each case calculated out as a composite factor made up of the percentage of gluten  $\times$  ratio of gliadin to glutenin (quality index).

## CANADIAN NORTHWEST WHEATS.

Locality.	Buyer's grade. <sup>1</sup>	Gliadin. Per cent.	Glutenin. Per cent.	Ratio of Gliadin to Glutenin.	Composite factor. Gluten ratio. Per cent.
Reston .....	2 H	7.32	4.43	1.65	19.38
Plum Coulee ..	1 N	5.4	3.61	1.49	13.42
Carman .....	1 H	7.77	3.30	2.34	25.90
Holland .....	2 H	5.73	4.0	1.43	13.91
Lauder .....	2 H	7.18	4.67	1.53	18.13
Virden (damp)	1 H	5.19	4.93	1.05	10.62
Lauder '97 ....	1 H	8.39	4.61	1.8	23.4
Franklin .....	1 N	6.14	4.53	1.35	14.40
Hartney .....	1 H	5.43	4.24	1.2	11.6
Dom. City .....	2 N	5.15	3.71	1.38	12.22
McDonald .....	1 N	5.51	5.08	1.08	11.43
Manitou .....	2 N	4.57	5.91	0.7	7.33
Altonia .....	1 H	6.53	4.25	1.54	16.60
Reston .....	1 H	7.7	4.88	1.57	19.75
Treesbank .....	1 H	7.36	5.0	1.47	18.16
Douglass .....	1 H	7.7	4.4	1.77	21.41
Qu'appelle ....	1 H	7.86	4.16	1.9	22.84
Souris .....	1 H	7.01	5.10	1.37	16.59
Indian Head ..	1 H	7.98	4.92	1.62	20.89
Sintaluta .....	1 H	8.14	5.2	1.56	20.81
Whitewater ...	1 H	6.12	5.44	1.12	12.95
Boissevain ....	1 H	6.46	4.84	1.33	15.02
Stohton .....	1 H	6.62	4.40	1.5	16.53
Rosenfeldt ....	1 H	5.14	5.04	1.0	10.18
Ninga .....	2 H	5.59	5.0	1.11	11.97
McGregor .....	1 N	6.02	4.88	1.23	13.40
Neepawa .....	1 N	4.76	4.64	1.0	9.4
Portage .....	...	6.7	4.92	1.36	15.66
Portage (damp) ..	..	6.4	6.08	1.05	13.10
Elkhorn .....	1 H	7.06	5.2	1.35	16.55
Thornhill .....	1 N	6.5	4.4	1.47	16.02
Fleming .....	1 H	7.50	5.09	1.47	18.52
Griswald .....	1 H	7.50	5.64	1.33	17.48
Mileta .....	1 H	8.18	5.04	1.6	21.15
Bagat .....	2 H	7.34	5.0	1.47	18.13
Alemeda .....	1 H	8.29	4.45	1.86	23.69
Stohton .....	L White Fife	6.6	4.7	1.4	15.82
Sintaluta .....	1 H	9.21	4.60	2.1	27.62
Methven .....	1 H	8.52	5.0	1.7	22.98
Elkhorn (damp) ..	..	8.13	4.64	1.75	22.34
Carroll .....	..	7.58	5.30	1.43	18.42
Indian Head ...	1 H	7.88	4.77	1.65	20.87

<sup>1</sup> Grades in descending. 1 Hard ; 2 Hard ; 1 Northern ; 2 Northern.

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**GLUTEN CONSTITUENTS OF WHEAT AND FLOUR. 267**

Locality.	Buyer's grade. <sup>1</sup>	Gliadin. Per cent.	Glutenin. Per cent.	Ratio of Gliadin to Glutenin.	Composite factor. Gluten ratio. Per cent.
Arden .....	1 N	5.07	5.49	0.92	9.71
Treesbank .....	1 H	8.76	4.82	1.81	24.57
Alemeda .....	1 White Fife	8.85	4.6	1.92	25.82
McGregor .....	2 H	6.44	4.36	1.47	15.87
Dauphin .....	1 N	4.25	4.25	1.0	8.5
Morden .....	1 N	3.65	3.65	1.0	7.3
Gretna .....	1 N	3.8	3.7	1.0	7.5
McDonald .....	2 H	5.8	4.0	1.45	13.21
Carberry .....	1 N	5.7	3.7	1.53	14.38
Moosomin .....	1 H	7.65	4.0	1.9	22.13
Treesbank .....	1 H	7.87	4.3	1.83	22.47
Neepawa .....	1 N	6.65	4.2	1.57	17.03
Indian Head ..	1 H	6.35	4.1	1.51	16.48
Carroll .....	1 H	6.7	4.1	1.63	17.60
Elva .....	2 H	7.6	3.95	1.92	22.17
Winkler .....	1 N	6.0	3.5	1.71	16.24
Altonia .....	1 N	7.5	4.1	1.82	21.11
Dom. City .....	2 N	5.4	3.7	1.46	13.28
Elkhorn(damp) ..		6.5	4.0	1.65	18.00
Elva .....	2 H	8.37	4.3	1.94	24.58
Reston .....	2 H	8.0	4.5	1.78	22.25
Douglass(damp) ..		6.65	4.2	1.58	17.13
Sintaluta .....	1 H	7.77	4.5	1.73	21.2
Boissevain .....	1 H	7.3	4.4	1.65	19.3
Qu'appelle .....	1 H	8.58	4.2	2.904	26.0
Manitou .....	2 Spring	4.0	4.2	0.95	7.78
Bagat .....	1 N	3.7	4.0	0.93	7.20
McGregor .....	1 N	4.65	4.10	1.1	9.62
Thornhill .....	1 N	5.4	4.2	1.3	12.48
Hamiota .....	1 H	7.15	4.6	1.54	18.10
Hartney .....	1 H	7.8	4.0	1.95	23.0
Treesbank .....	..	8.37	4.0	2.09	25.85
Indian head ...	..	7.51	4.1	1.83	21.24
Carman .....	..	7.77	3.6	2.14	24.18
Douglass .....	..	7.8	3.8	2.0	23.2
Bagat .....	..	7.0	4.2	1.66	18.59
Holland .....	..	6.1	4.4	1.4	14.7
Methven .....	..	8.1	4.0	2.02	24.44

<sup>1</sup> Grades, in descending order : 1 Hard ; 2 Hard ; 1 Northern ; 2 Northern.

## CANADIAN NORTHWEST AND OTHER FLOURS.

Name of flour.	Grade. <sup>1</sup>	Gliadin. Per cent.	Glutenin. Per cent.	Ratio of gliadin to glutenin.	Composite factor. Per cent. gluten X ratio.
Keewatin	Patent .....	8.13	2.24	3.62	37.54
"	Baker's .....	8.47	3.90	2.17	26.84
"	Algoma .....	7.98	4.55	1.75	21.92
"	Glenwood .....	7.2	5.53	1.3	16.54
Portage	Patent .....	8.4	2.1	4.0	42.00
"	Baker's .....	8.65	2.6	3.32	37.25
"	Algoma .....	8.2	3.2	2.59	29.78
"	Glenwood .....	8.0	4.7	1.7	21.69
Keewatin	Patent .....	8.9	1.60	5.56	58.38
"	Baker's .....	8.14	3.52	2.3	26.81
"	Algoma .....	7.46	4.80	1.6	19.61
"	Glenwood .....	6.90	5.90	1.2	15.38
Austria-Hungary (best) .....		9.38	2.80	3.35	40.80
Keewatin	Patent .....	8.25	2.0	4.12	42.23
"	Baker's .....	9.06	2.25	4.02	45.46
"	Algoma .....	8.63	3.24	2.66	31.57
"	Patent .....	9.0	1.9	4.73	51.55
"	Baker's .....	8.65	3.2	2.7	32.0
"	Algoma .....	8.5	3.8	2.23	27.42
"	Glenwood .....	8.1	4.9	1.65	21.45
"	Patent .....	7.95	2.85	2.78	30.02
"	Baker's .....	8.1	3.1	2.61	29.23
Ogilvie	Patent . . . . .	8.04	2.92	2.76	30.24
"	Baker's .....	7.4	3.6	2.05	22.55

At the present stage of progress in these investigations, it cannot be stated that these ratios, or the calculated factors, are true indices of the bread-making qualities and values of the different wheats and flours, but it is certain that there is a direct and very intimate connection between the same.

The subject is one worthy of attention by industrial chemists, and it is quite possible that in time the buying, mixing, and milling of wheats may come under as definite chemical control as are, at present, similar operations, with respect to the smelting of ores.

LABORATORY OF THE OTTAWA GOLD MILLING AND  
MINING CO., KEEWATIN, ONTARIO, March 6, 1900.

<sup>1</sup> Grades in descending scale: Patent, Baker's, Algoma, Glenwood.

# LIME AND SULPHURIC ACID BY THE PHOTOMETRIC METHOD.

BY J. I. D. HINDS.

Received March 30, 1900.

IN this Journal, 18, 661, I gave the results of some investigations looking to the rapid determination of lime and sulphuric acid by means of the opacity of the precipitates produced in the usual way. Since then I have had occasion to make frequent tests of the accuracy of the method and am able to give some interesting results.

The only apparatus needed is the photometric cylinder made of glass. It is 3.5 centimeters wide and 20 centimeters high, and is graduated in centimeters and millimeters from the inside of the bottom for the convenient reading of the depth of the liquid in the cylinder. It is used with an ordinary sperm or wax candle. The cylinder is held over the lighted candle and the water containing the precipitate is poured into the cylinder until the image of the flame just disappears. The depth is read and the per cent. is calculated from the equation or read from a table. The lime is precipitated with solid calcium oxalate and the sulphuric acid with solid barium chloride. The equations used are as follows :

$$\text{For CaCO}_3, y = \frac{0.0642}{x - 0.3}; \quad \text{For CaO, } y = \frac{0.0360}{x - 0.3};$$

$$\text{For H}_2\text{SO}_4, y = \frac{0.0590}{x}; \quad \text{For SO}_3, y = \frac{0.0482}{x};$$

in which  $x$  is the reading of the cylinder and  $y$  the per cent. sought. For the details of the method, see the article above referred to. A table computed from these equations is appended to this article.

Near the university building in Lebanon is a bored well yielding a limestone water, analysis of which shows that it contains among other things

Calcium carbonate about	16.00	parts in	100,000
Magnesium “ “	13.00	“ “	100,000
Magnesium sulphate “	16.00	“ “	100,000
Total solids	60.80	“ “	100,000

I made a series of photometric and gravimetric determinations of the lime and sulphuric acid in this water from day to day, with the following results :

Calcium carbonate—parts in 100,000.

	1.	2.	3.	4.	5.	6.	7.
Photometric.....	16.5	15.7	15.7	16.5	15.7	22.2	19.5
Gravimetric .....	16.4	16.0	15.5	16.0	15.5	22.4	19.0
Difference.....	0.1	0.3	0.2	0.5	0.2	0.2	0.5

Sulphuric acid—parts in 100,000.

	1.	2.	3.	4.	5.
Photometric .....	13.1	11.8	5.7	7.9	4.9
Gravimetric .....	13.2	11.4	5.4	7.2	4.7
Difference .....	0.1	0.4	0.3	0.7	0.2

These differences, omitting the decimal point, mean parts in a million of the water and are a reasonably small fraction of the total amount present. For sanitary and technical purposes the photometric determinations are just as good as those made in the regular way. When we consider that one of these determinations can be made in five minutes and that the method is adapted to many other substances, it seems to be worthy of the attention and careful investigation of chemists. It is much more accurate than many of the approximate methods now in use and requires no previous preparation in the way of standard solutions.

I have found the method practicable in the determination of the lime in carbonates. I give one example. A sample of clayey limestone containing 16.14 per cent. of calcium carbonate gave by this method 16.46 per cent. The determination was made as follows: Dissolved 0.1081 gram of the limestone in hydrochloric acid with a few drops of nitric acid, evaporated to dryness in a porcelain dish over a free flame, added water with a little hydrochloric acid, filtered, neutralized with ammonia, made up to 150 cc., then tested in the usual way. The reading in the cylinder was 6.0 cm. Substituting this for  $x$  in the equation we find the solution to contain 0.0112 per cent. of calcium carbonate. The calculation is then made as follows :

$$\begin{array}{l} 100 \text{ cc. contain } 0.0112 \text{ gram CaCO}_3, \\ 150 \text{ " " " } 0.0178 \text{ " " " } \end{array}$$

0.1081 gram of the sample contains 0.0178 gram  $\text{CaCO}_3$ , or



16.46 per cent. The whole operation can be performed within a half hour.

The determination of sulphuric acid in urine is very easy and rapid. Five or ten cc. of the urine are measured from a burette or pipette, made slightly acid with hydrochloric acid, and diluted to 100 cc. Barium chloride is added and the reading taken. Two trials with a urine diluted from 10 to 100 cc. gave the same reading; *viz.*, 3.0 cm. This corresponds to 0.0197 per cent.  $\text{H}_2\text{SO}_4$ . Multiplying by 10 we have 0.197 as the per cent. of  $\text{H}_2\text{SO}_4$  in the urine.

To save the trouble and labor of computation I have prepared the accompanying table from which the percentages can be directly taken as soon as the reading is made.

TABLE FOR PHOTOMETRIC DETERMINATION OF LIME AND SULPHURIC ACID.

$y$  equals the per cent. desired, and  $x$  is the reading of cylinder in centimeters. For parts in 100,000 remove the decimal point three places to the right.

	Per cent. $\text{CaCO}_3$ .	Per cent. $\text{CaO}$ .	Per cent. $\text{H}_2\text{SO}_4$ .	Per cent. $\text{SO}_3$ .
$x$ .	$y = \frac{0.0642}{x-0.3}$ .	$y = \frac{0.0360}{x-0.3}$ .	$y = \frac{0.0590}{x}$ .	$y = \frac{0.0482}{x}$ .
1.0	0.0917	0.0514	0.0590	0.0482
1.1	0.0802	0.0450	0.0536	0.0438
1.2	0.0713	0.0400	0.0492	0.0402
1.3	0.0642	0.0360	0.0454	0.0371
1.4	0.0583	0.0327	0.0421	0.0344
1.5	0.0534	0.0300	0.0393	0.0322
1.6	0.0494	0.0277	0.0370	0.0301
1.7	0.0456	0.0257	0.0347	0.0283
1.8	0.0428	0.0240	0.0328	0.0268
1.9	0.0401	0.0225	0.0311	0.0254
2.0	0.0377	0.0212	0.0295	0.0241
2.1	0.0356	0.0201	0.0281	0.0230
2.2	0.0338	0.0190	0.0268	0.0219
2.3	0.0321	0.0180	0.0257	0.0210
2.4	0.0306	0.0172	0.0246	0.0201
2.5	0.0292	0.0164	0.0236	0.0193
2.6	0.0279	0.0156	0.0227	0.0185
2.7	0.0268	0.0150	0.0218	0.0179
2.8	0.0257	0.0144	0.0211	0.0172
2.9	0.0247	0.0138	0.0203	0.0166
3.0	0.0238	0.0133	0.0197	0.0161
3.1	0.0229	0.0129	0.0190	0.0156
3.2	0.0221	0.0124	0.0184	0.0151

	Per cent. $\text{CaCO}_3$ .	Per cent. $\text{CaO}$ .	Per cent. $\text{H}_2\text{SO}_4$ .	Per cent. $\text{SO}_3$ .
$x$ .	$y = \frac{0.0642}{x - 0.3}$ .	$y = \frac{0.0360}{x - 0.3}$ .	$y = \frac{0.0590}{x}$ .	$y = \frac{0.0482}{x}$ .
3.3	0.0214	0.0120	0.0179	0.0146
3.4	0.0207	0.0116	0.0174	0.0142
3.5	0.0201	0.0112	0.0169	0.0138
3.6	0.0195	0.0109	0.0164	0.0134
3.7	0.0189	0.0106	0.0159	0.0130
3.8	0.0183	0.0103	0.0155	0.0127
3.9	0.0178	0.0100	0.0151	0.0124
4.0	0.0173	0.0097	0.0147	0.0121
4.1	0.0169	0.00947	0.0144	0.0118
4.2	0.0165	0.00923	0.0141	0.0115
4.3	0.0161	0.00900	0.0137	0.0112
4.4	0.0157	0.00878	0.0134	0.0110
4.5	0.0153	0.00857	0.0131	0.0107
4.6	0.0149	0.00837	0.0128	0.0105
4.7	0.0146	0.00818	0.0125	0.0103
4.8	0.0143	0.00800	0.0123	0.0101
4.9	0.0140	0.00782	0.0120	0.00983
5.0	0.0137	0.00766	0.0118	0.00964
5.1	0.0134	0.00750	0.0116	0.00945
5.2	0.0131	0.00735	0.0113	0.00927
5.3	0.0128	0.00720	0.0111	0.00909
5.4	0.0126	0.00706	0.0109	0.00992
5.5	0.0123	0.00692	0.0107	0.00876
5.6	0.0121	0.00679	0.0105	0.00861
5.7	0.0119	0.00667	0.0104	0.00845
5.8	0.0117	0.00654	0.0102	0.00831
5.9	0.0115	0.00643	0.0100	0.00817
6.0	0.0113	0.00632	0.00983	0.00804
6.1	0.0111	0.00621	0.00967	0.00790
6.2	0.0109	0.00610	0.00952	0.00777
6.3	0.0107	0.00600	0.00937	0.00765
6.4	0.0105	0.00590	0.00922	0.00753
6.5	0.0104	0.00580	0.00908	0.00742
6.6	0.0102	0.00571	0.00894	0.00730
6.7	0.01003	0.00562	0.00881	0.00719
6.8	0.00988	0.00554	0.00868	0.00709
6.9	0.00973	0.00545	0.00855	0.00698
7.0	0.00958	0.00537	0.00843	0.00689
7.1	0.00944	0.00529	0.00831	0.00679
7.2	0.00930	0.00522	0.00820	0.00669
7.3	0.00917	0.00514	0.00808	0.00660
7.4	0.00904	0.00507	0.00797	0.00651
7.5	0.00892	0.00500	0.00787	0.00642
7.6	0.00879	0.00493	0.00776	0.00634

	Per cent. $\text{CaCO}_3$ .	Per cent. $\text{CaO}$ .	Per cent. $\text{H}_2\text{SO}_4$ .	Per cent. $\text{SO}_3$ .
$x$ .	$y = \frac{0.0642}{x - 0.3}$ .	$y = \frac{0.0360}{x - 0.3}$ .	$y = \frac{0.0590}{x}$ .	$y = \frac{0.0482}{x}$ .
7.7	0.00867	0.00486	0.00766	0.00626
7.8	0.00856	0.00480	0.00756	0.00618
7.9	0.00845	0.00474	0.00747	0.00610
8.0	0.00834	0.00468	0.00737	0.00602
8.1	0.00823	0.00462	0.00728	0.00595
8.2	0.00813	0.00456	0.00720	0.00588
8.3	0.00802	0.00450	0.00711	0.00581
8.4	0.00792	0.00444	0.00702	0.00574
8.5	0.00783	0.00439	0.00694	0.00567
8.6	0.00773	0.00434	0.00686	0.00560
8.7	0.00764	0.00429	0.00678	0.00554
8.8	0.00755	0.00424	0.00670	0.00548
8.9	0.00746	0.00419	0.00663	0.00541
9.0	0.00738	0.00414	0.00655	0.00536
9.1	0.00730	0.00409	0.00648	0.00530
9.2	0.00721	0.00404	0.00641	0.00524
9.3	0.00713	0.00400	0.00634	0.00518
9.4	0.00705	0.00396	0.00628	0.00513
9.5	0.00698	0.00391	0.00621	0.00507
9.6	0.00690	0.00387	0.00615	0.00502
9.7	0.00683	0.00383	0.00608	0.00497
9.8	0.00676	0.00379	0.00602	0.00492
9.9	0.00669	0.00375	0.00596	0.00487
10.0	0.00662	0.00371	0.00590	0.00482
10.1	0.00655	0.00367	0.00584	0.00477
10.2	0.00648	0.00364	0.00578	0.00473
10.3	0.00642	0.00360	0.00573	0.00468
10.4	0.00636	0.00357	0.00567	0.00463
10.5	0.00629	0.00353	0.00562	0.00459
10.6	0.00623	0.00350	0.00557	0.00455
10.7	0.00617	0.00346	0.00551	0.00451
10.8	0.00611	0.00343	0.00546	0.00447
10.9	0.00606	0.00340	0.00541	0.00442
11.0	0.00600	0.00336	0.00536	0.00438
11.1	0.00594	0.00333	0.00532	0.00434
11.2	0.00589	0.00330	0.00528	0.00430
11.3	0.00584	0.00327	0.00523	0.00426
11.4	0.00578	0.00324	0.00518	0.00423
11.5	0.00573	0.00321	0.00513	0.00419
11.6	0.00568	0.00318	0.00508	0.00415
11.7	0.00563	0.00316	0.00504	0.00412
11.8	0.00558	0.00313	0.00500	0.00408
11.9	0.00553	0.00310	0.00496	0.00405
12.0	0.00548	0.00308	0.00492	0.00401

	Per cent. $\text{CaCO}_3$ .	Per cent. $\text{CaO}$ .	Per cent. $\text{H}_2\text{SO}_4$ .	Per cent. $\text{SO}_3$ .
$x$ .	$y = \frac{0.0642}{x-0.3}$ .	$y = \frac{0.0360}{x-0.3}$ .	$y = \frac{0.0590}{x}$ .	$y = \frac{0.0482}{x}$ .
12.1	0.00543	0.00305	0.00488	0.00398
12.2	0.00539	0.00303	0.00484	0.00395
12.3	0.00535	0.00300	0.00480	0.00392
12.4	0.00531	0.00298	0.00476	0.00389
12.5	0.00526	0.00295	0.00472	0.00386
12.6	0.00522	0.00293	0.00468	0.00383
12.7	0.00517	0.00290	0.00465	0.00380
12.8	0.00513	0.00288	0.00461	0.00377
12.9	0.00509	0.00285	0.00457	0.00374
13.0	0.00505	0.00283	0.00454	0.00371
13.2	0.00498	0.00279	0.00447	0.00364
13.4	0.00490	0.00275	0.00440	0.00359
13.6	0.00483	0.00271	0.00434	0.00354
13.8	0.00476	0.00267	0.00427	0.00349
14.0	0.00469	0.00263	0.00421	0.00344
14.2	0.00462	0.00259	0.00415	0.00339
14.4	0.00455	0.00255	0.00410	0.00335
14.6	0.00449	0.00251	0.00404	0.00330
14.8	0.00443	0.00248	0.00399	0.00326
15.0	0.00437	0.00245	0.00393	0.00321
15.5	0.00422	0.00237	0.00381	0.00311
16.0	0.00409	0.00229	0.00369	0.00301
16.5	0.00396	0.00222	0.00358	0.00292
17.0	0.00384	0.00216	0.00347	0.00284
17.5	0.00373	0.00209	0.00337	0.00276
18.0	0.00363	0.00203	0.00328	0.00268
18.5	0.00353	0.00198	0.00319	0.00261
19.0	0.00343	0.00192	0.00311	0.00254
19.5	0.00334	0.00187	0.00303	0.00247
20.0	0.00326	0.00183	0.00295	0.00241

UNIVERSITY OF NASHVILLE.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA  
UNIVERSITY, No. 22.]

## UPON BISMUTH COBALTICYANIDE.

BY J. A. MATHEWS.

Received April 28, 1900.

IN a recent article entitled "A Preliminary Study of the Cobalticyanides,"<sup>1</sup> by E. H. Miller and myself, mention was made of bismuth cobalticyanide. It was stated that "the original precipitate seems to be a normal cobalticyanide, but it has not been analyzed and no mention of such a compound is found in the

<sup>1</sup> This Journal, 22, 65 (1900).

literature.' It was further stated that as lead cobalticyanide is exceedingly soluble in water, there might be a possibility of effecting a separation of bismuth from lead in pig-leads by the use of potassium cobalticyanide. I have analyzed the cobalticyanide of bismuth, noted carefully its properties, and determined the most favorable conditions for its precipitation. The results have not been favorable to its use in the analysis of pig-leads but it may still be found useful in the analysis of lead-bismuth alloys, "fusible metals" such as Wood's alloy, etc.

The precipitate of bismuth cobalticyanide is crystalline, settles and filters well, and contains more or less water which is not completely given up below  $165^{\circ}\text{C}$ . The anhydrous compound has the formula  $\text{BiCo}(\text{CN})_6$ . The theoretical percentage of bismuth for this compound is 49.17. The average of three determinations gave 49.05 per cent. bismuth. When freshly precipitated and before filtering, the precipitate appears white but on the filter it has a slight greenish tint. During the process of dehydrating the color becomes blue, getting darker as the temperature rises; then upon exposure to the air it reabsorbs water rapidly and the color becomes pink. This behavior seems to indicate some decomposition of the cobalticyanide radical at the temperature required for complete dehydration, and this view is strengthened by the fact that different samples exhibit differences of tint and that, in general, after exposing the anhydrous samples to the air, the depth of the pink tint is proportional to the depth of blue in the sample exposed.

A sample of bismuth cobalticyanide dried below  $100^{\circ}\text{C}$ . and exposed to the air for one week, lost by subsequent heating to  $162^{\circ}\text{C}$ ., 19.5 per cent. Two portions dried to constant weight at  $100^{\circ}\text{C}$ . lost, by heating to  $165^{\circ}\text{C}$ ., 4.35 per cent. and 4.24 per cent. respectively, corresponding to one molecule of water. The samples upon exposure to the air reabsorbed about 16.25 per cent. of water, the actual percentage fluctuating slightly from day to day.

*Completeness of the Precipitation.*—By means of several series of experiments in which bismuth solutions were precipitated by potassium cobalticyanide, it was found that below a concentration of 0.0079 gram of bismuth per cubic centimeter the precipitate was under no conditions complete and that at ten times

that dilution no precipitate was produced even on long standing. By varying the ratio of bismuth to potassium cobalticyanide, it was shown that a decided excess of the latter was beneficial. The precipitation is found to be more complete if acetic acid is present. Boiling assists in the precipitation of very dilute solutions, but a solution so dilute that no precipitate forms in the cold is never completely precipitated by heating. The solubility of the precipitate does not vary much with change of temperature, and when once formed is not soluble in a quantity of water which would have prevented its formation in the beginning.

The following tables, with the remarks accompanying each, show the influence of different conditions upon the completeness of precipitation. A solution containing 0.0794 gram of bismuth per cubic centimeter in nitric acid was used in all cases.

I. VARYING RATIO OF  $\text{Bi}(\text{NO}_3)_3$  TO  $\text{K}_3\text{Co}(\text{CN})_6$ .

	Temperature.	$\text{Bi}(\text{NO}_3)_3$ cc.	Half-normal $\text{K}_3\text{Co}(\text{CN})_6$ cc.
1	cold	5	15
2	"	3	15
3	"	1	15
4	hot	5	15
5	"	3	15
6	"	1	15

All filtrates showed a trace of bismuth with  $(\text{NH}_4)_2\text{S}$ : Greater in 4, 5, and 6, than in 1, 2, and 3; deepest in 1 and 4; least in 3 and 6, respectively. The insolubility is therefore increased by an excess of  $\text{K}_3\text{Co}(\text{CN})_6$ .

II. VARYING VOLUME. RATIO OF  $\text{Bi}(\text{NO}_3)_3$  :  $\text{K}_3\text{Co}(\text{CN})_6$  CONSTANT.

	$\text{Bi}(\text{NO}_3)_3$ cc.	$\text{H}_2\text{O}$ cc.	$\text{K}_3\text{Co}(\text{CN})_6$ cc.
1	5	5	15
2	3	7	9
3	1	9 (+ $\text{H}\bar{\text{A}}$ )	3 also,
[4	1	9	6]

Number 3 is very incomplete. Filtrate gave large precipitate with ammonium carbonate. 1, 2, and 4 showed only a trace of bismuth with  $(\text{NH}_4)_2\text{S}$ . Comparison of 3 and 4 shows the effect of increasing the amount of  $\text{K}_3\text{Co}(\text{CN})_6$ .

## III. CONSTANT VOLUME.

	$\text{Bi}(\text{NO}_3)_3$ cc.	$\text{H}_2\text{O}(+\text{H}\bar{\text{A}})$ cc.	$\text{K}_3\text{Co}(\text{CN})_6$ cc.
1	5	5	15
2	3	12	10
3	1	19	5
4	1	21	3

In 1, 2, and 3 the ratio of  $\text{K}_3\text{Co}(\text{CN})_6$  to  $\text{Bi}(\text{NO}_3)_3$  increases with the dilution. Filtrate from 3 contained 10 per cent. of bismuth; filtrate from 4 contained 57 per cent. of the bismuth. \*In 1 and 2, the filtrates showed a trace of bismuth with  $(\text{H}_2\text{S})_2\text{S}$ , greater in 2 than in 1, showing that the completeness of the precipitation increases with the concentration.

### RAPID METHOD FOR THE DETERMINATION OF CARBON IN IRON OR STEEL BY COMBUSTION.

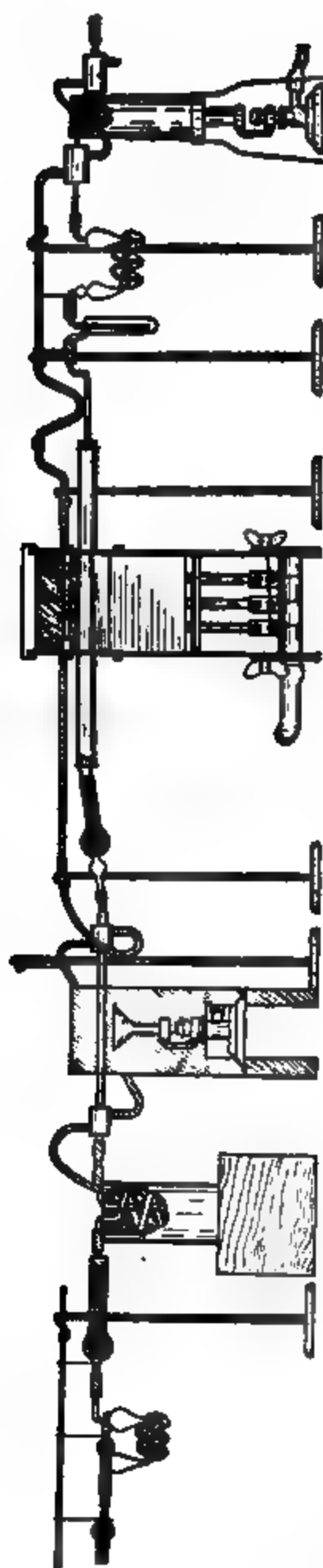
BY GEO. WM. SARGENT.

Received April 5, 1900.

THE part taken by the carbon in determining the utility of steel or iron, especially the effect of slight changes in the quantity, impresses one with the need of exercising the greatest care that its estimation may be accurately made, and yet the large number of determinations required in a limited time calls for a greater speed in their accomplishment.

The color method of Eggertz is probably the most rapid, but its application is so limited that it is scarcely used outside of small furnace work where straight steels only are encountered, and where the steel has undergone the same treatment, consequently the carbon is present in always the same condition. The advent of alloys of nickel, chromium, tungsten, molybdenum, titanium, and, with iron, forces even the furnace chemist back to the most reliable method,—that of the combustion, in oxygen, of the carbon due from the solution of the drillings. During the past three months the results obtained in this laboratory, by this method somewhat modified, have been so eminently gratifying with regard to accuracy, rapidity, and simplicity of the apparatus used, that I believe it worthy the attention of other chemists.

The apparatus as shown by the accompanying cut consists of, on the right, a small copper or platinum spiral, water-jacketed at each end to prevent the burning of the rubber con-



nections, and suspended in a copper cylinder over a burner; a Geissler potash bulb, followed by an empty "safety" tube, then the porcelain tube resting in a three-burner combustion furnace; a glass tube filled with coarse, wet sand; a copper tube filled with copper oxide and also water-jacketed at each end; a tin can containing a copper worm; then a 6-inch calcium chloride tube; the weighed potash bulb and its calcium chloride tube; and finally the guard.

It will be best to describe in detail each portion of the apparatus and its function.

The spiral is made from a platinum tube 17 inches long and  $\frac{5}{8}$  inch in diameter. This gives four close coils  $\frac{1}{4}$  inch in diameter and leaves 4 inches extend on either side. The water-jackets are two pieces of  $\frac{1}{2}$  inch copper tubing  $1\frac{1}{2}$  inches long, closed at the ends by rivet burrs, carefully soldered and containing an outlet and an inlet, the outlet of the one being connected to the inlet of the other by a  $\frac{1}{4}$  inch copper tube bent around the support. The latter is a  $1\frac{1}{2}$  inch copper tube with  $\frac{1}{8}$  inch walls, 6 inches long, resting on three legs sufficiently long to bring the spiral the proper distance from the burner. A two-way cock leads the oxygen or air from the tanks to the spiral where any hydrocarbons are burned. The resulting carbon dioxide is caught in the Geissler potash bulb to which the spiral is connected by rubber tubing, thence the purified oxygen or air passes through the empty tube which is used to catch any potassium hydroxide from the Geissler bulb, into the combustion tube. Both the potash



bulb and the "safety" are suspended from the small copper pipe conveying the water from the outlet of the second water-jacket to the first jacket on the copper oxide tube. The combustion tube is a  $\frac{1}{2}$  inch glazed porcelain tube 16 inches long, 10 inches of which extend on either side of the combustion furnace. The curved piece of fire-brick protects the tube from direct contact with the flames of the furnace. The latter is 5 inches long, having but 3 burners and was made from an old 10-burner furnace. To prevent the boat holding the carbon from being pushed into the combustion tube beyond the heated portion, a piece of clay pipe stem is placed at one end. The gases from the combustion tube pass through the coarse, wet sand loosely packed in a  $\frac{1}{2}$  inch glass tube 6 inches long and held in place by two small disks of copper gauze placed at either end. This moist sand and the copper disks effectually hold any hydrochloric acid or chlorine that the gases may contain. The copper oxide tube is a straight piece of copper  $\frac{1}{2}$  inch in diameter, 1 foot long, water-jacketed at each end, the water flowing from the outlet of the first jacket to the second, and thence into the tin can containing the worm. The copper oxide tube rests on a support of sheet tin, bent as shown in the cut, and slit at each side and at the bottom of the back, the two side openings supporting the copper tube, while the one in the back allows the gas pipe to enter to the burner, which has a spreader so that the copper oxide is heated for a distance of at least 3 inches. The worm consists of 3 very loose coils of  $\frac{1}{4}$  inch copper tubing. A piece of tube about 20 inches long will make about the right size worm. From the cooler, the gases are dried by passing through 6 inches of thoroughly dehydrated calcium chloride. They then enter the weighed potash bulb and its calcium chloride tube, which are in one piece. These bulbs are extra large at the part holding the potash solution, being 1 inch long and  $\frac{1}{2}$  inch wide, weighing, when filled for use, about 75 grams, and holding 30 cc. caustic potash solution. They, therefore, allow the gases to come in contact with more of the solution for a longer time.<sup>1</sup> The guard tube is the usual calcium chloride tube. It is absolutely essential that all the calcium chloride used should be thoroughly dehydrated, that none of the fine powder

<sup>1</sup> These bulbs were made to order by Queen & Co., Philadelphia.

be placed in the tubes, particularly that one attached to the weighed potash bulb, and that as little of the space within the tubes as is possible be taken up with cotton, which does no good as an absorbent. It is best to sift out the fine powder from the dehydrated calcium chloride and take that which is about  $\frac{1}{8}$  inch diameter, or the size of a dried pea.

The apparatus being ready, the combustion is proceeded with as follows :

A stream of water is started through the water-jackets, the burners under the spiral and copper oxide lighted, also the 3 burners of the furnace, which are regulated so the tips of the flames just touch the curved fire-brick upon which the porcelain tube rests. After ten minutes the burners may be turned on sufficiently far to bring that part of the tube within the furnace to a red heat and hold it there. The water overflowing from the can should be about  $15^{\circ}\text{C}$ . The weighed potash bulb having been connected, a current of air is started through the apparatus at the rate of about 5 bubbles per second in the weighed bulb (this is a little faster than one can count), the stopper at the forward end of the combustion tube is withdrawn and, as quickly as possible, the platinum boat containing the carbon residue obtained by the standard method of solution of steel, is pushed into the tube until it meets the pipe stem, and the stopper immediately replaced. The air is then turned off and replaced by a current of oxygen at a slightly slower rate of speed, about  $4\frac{1}{2}$  bubbles per second. At the expiration of ten minutes the oxygen is turned off and the air on at the former speed for ten minutes. The connections are then broken, a new weighed potash bulb placed in the train; a fresh boat containing the carbon is inserted after removing the first one and a new combustion proceeded with. The boats should be taken from the oven, which is kept at  $100^{\circ}\text{C}$ ., and at once put into the porcelain tube in order to prevent a cold boat cracking the tube.

The copper oxide is always kept at a red heat, as is also the combustion tube, as long as the apparatus is in use, from the beginning of the day's work until its completion.

A combustion is thus made in twenty minutes, and one man, with two of these pieces of apparatus side by side so arranged that when the oxygen or air is turned from one it goes on to the

her, and six potash bulbs, can make 48 combustions per day in nine hours.

After each day's work it is necessary to wash the sand in the tube by running a stream of water through it; remove any moist calcium chloride from the tube next the cooler and replace it with fresh or, better still, put in an entirely new tube full of freshly dehydrated calcium chloride and dry the moist one to have it ready for use the day following. The worm also should be dried out about every two days by placing it over a burner and blowing air through it.

In our practice we have found that about 25 combustions can be made on each bulb before it will need refilling with calcium chloride and caustic potash solution. If more than this number be run on a bulb it will be found that the calcium chloride has ceased to catch all the moisture carried from the potash solution. The latter has a specific gravity of 1.27 and is capable of absorbing 2.5 grams of carbon dioxide with perfect safety.

I append some of the results obtained by the above method of combustion and by combustion in a platinum tube.

Sample No	Combustions in a platinum tube. Per cent. carbon.	Combustions in a porcelain tube by new method. Per cent. carbon.
16 .....	0.836	0.832
17 .....	0.850	0.860
17 .....	....	0.864
17 .....	....	0.864
1238 B C 389 .....	0.563	0.566
1238 B C 389 .....	....	0.552
1580 .....	1.111	1.108
1099 C .....	1.087	1.075
1099 C .....	1.073	....
1078 C 291 .....	1.162	1.168
1078 C 291 .....	....	1.164
1060 C 283 .....	0.326	0.323
R. J. ....	0.958	0.958
R. J. ....	0.955	0.953
R. J. ....	0.953	0.955
J. ....	1.067	1.068 <sup>1</sup>
J. ....	1.070	....
B. ....	0.904	0.900 <sup>1</sup>

<sup>1</sup> These results were obtained when exhibiting the apparatus before the Philadelphia Section of the American Chemical Society; the carbon content of the steel was unknown to me at that time. The results obtained by combustion in a platinum tube are those of R. Job, chemist of the Philadelphia and Reading Railway Co., also of A. A. Blair.

Some duplicate results obtained by combustion in a porcelain tube by the new method are :

Sample No.	Carbon Per cent.
I .....	0.839
I .....	0.839
5 .....	0.838
5 .....	0.832
8 .....	0.776
8 .....	0.779
9 .....	0.850
9 .....	0.855
11 .....	0.843
11 .....	0.842
14 .....	0.848
14 .....	0.853
713 .....	1.012
713 .....	1.019
B X .....	1.608
B X .....	1.614

The condenser or worm cools the gases so that when they reach the weighed potash bulb, there is no tendency to carry out moisture while running the bubbles at the speed of five per second. In fact, blanks have shown that the gases can pass through the potash bulb at a speed so great that the bubbles are scarcely to be distinguished and no loss in weight will be sustained.

	Gain or loss in weight of bulb.	Number of bubbles per second.
Blank .....	0.0000	5
" .....	0.0000	5+
" .....	+0.0003	steady stream

Two weighed potash bulbs placed one after the other and a combustion of a high carbon steel made with the oxygen running five bubbles per second and the air a trifle faster, gave the following :

Sample No.		Before. Grams.	After. Grams.	Difference. Grams.
1905 B X 347	Weight of 1st bulb	17.4991	17.5920	0.0929
1905 B H 347	" of 2nd "	23.0177	23.01755	0.00015

A factor weight, 2.7272 grams, of the drillings was taken.

The porcelain tube may be replaced with a copper tube 16 inches long,  $\frac{5}{8}$  inch in diameter, and  $\frac{1}{8}$  inch walls, water-jacketed each end for  $1\frac{1}{2}$  inches, as these results show :

Sample	Combustion in a porcelain tube Per cent. carbon.	Combustion in a copper tube. Per cent. carbon
Standard No. 1.....	0.529	0.529
" " 1.....	0.529 <sup>1</sup>	0.527
" " 2.....	0.544	0.545

The copper tube, however, burns out in about two weeks, while the porcelain tube, with proper care, will last for weeks, especially if at the heated portion, the boat be kept from direct contact with the tube by a sheet of platinum foil.<sup>1</sup>

The life of the copper oxide tube is about three months. When it is burned out, however, it is quickly replaced, by another, the water-jackets being easily melted from the old tube and soldered on the new.

The whole apparatus can be made in any laboratory at a very small cost.

Mr. Job, who now has this apparatus in use in the laboratory of the Philadelphia and Reading Railway Co., has obtained very good results, a few of which he kindly gave me.

	Combustion in porcelain tube. Old method. Per cent. carbon.	New method. Per cent. carbon.
Standard No. 1.....	1.070	1.068
" " 3.....	0.937	0.937-0.942
" " 2.....	0.527	0.531
Blank.....	....	0.0000
" .....	....	0.0000

It may be stated that in almost every instance where blanks have been made, the difference in weight of the potash bulb has been zero. This is due, I believe, to the cooler, which permits the gases to pass into the potash bulb at the same temperature, or a slightly lower one, at which it leaves it; consequently the gas is saturated with moisture to the same degree. For this reason, I believe the accuracy of the determinations even exceeds the results obtained by the old method where a dry train is used. Many of the results that have been given, that is, those coming from this laboratory, have been made in the course of our everyday work by a man turning out a result every ten minutes from two of these pieces of apparatus, and they certainly show that,

<sup>1</sup> Old method combustion in platinum tube.

<sup>2</sup> Since the foregoing was written, Mr. Job has informed me that he has obtained excellent results by using a hard glass tube protected from the flames by a piece of iron, and supporting the boat within the tube in a sheet of platinum foil.

When at this rapid rate, the accuracy attained equals that of the more slow and painstaking method of combustion in a platinum tube.

It may be of interest to know that the copper oxide may be replaced by the electric spark as an oxidant to insure the complete change of the carbon to carbon dioxide. The action of the electric spark on a mixture of carbon monoxide and air, in the presence of moisture, is to produce carbon dioxide, ozone, and a very small amount of nitric acid; therefore, I removed the copper oxide from the system and placed in its stead a small glass tube through which two platinum wires were fused so that a spark would be produced between the points when a current from a Ruhmkorff coil passed through the wires. Combustions were then made as usual, except that during the time of burning in oxygen, a continuous stream of sparks played between the platinum wires within the tube. The following table shows the results obtained:

Sample No.	Method.	Weight of carbon dioxide Grams.	Carbon. Per cent.
1.30 Standard	Electric spark as oxidant	0.1303	1.303
1257 B D	" " " "	0.0720	0.720
1257 B D	No oxidant	0.0614	0.614
1257 B D	CuO as oxidant—combustion in platinum tube	0.0724	0.724
1254 B D	ditto	0.0747	0.747
1254 B D	Electric spark as oxidant	0.0744	0.744
Pig iron	" " " "	0.4193	4.193
Pig iron	CuO as oxidant—combustion in platinum tube	0.2060	4.120*

Starch paper moistened with potassium iodide and placed just before the weighed absorption bulb was turned blue, showing the presence of ozone.

Owing to the platinum contacts of the induction coil becoming worn away with continued use and the consequent stoppage of the sparks, thus creating error, the hot copper oxide is preferred as an oxidant. Could, however, the trouble with the induction coil be simply remedied, the apparatus without the copper oxide would be the neatest, cleanest, and most compact to use.

Mr. John K. Faust has made most of the determinations in-

\* In every case except that marked with an asterisk, where a half factor weight was taken, a whole factor weight, 2.7272 grams, was taken.

lved in perfecting this method of carbon combustions, and its success is largely due to his careful work, for which I sincerely thank him. I also wish to thank Mr. F. Cooper Pullman for his assistance in working up the electric spark as an oxidant.

LABORATORY OF THE CARPENTER STEEL CO., READING, PA.

## SOIL HUMUS. SOME SOURCES OF ERROR IN ANALYTICAL METHODS.

BY A. L. EMERY.

Received April 21, 1900.

DURING the past four years we have devoted considerable time in our laboratory to the analysis of California and Hawaiian soils for the purpose of determining the kind of fertilizer best adapted for each separate piece or tract of land. The analytical methods of Dr. E. W. Hilgard have been generally followed in our work and good results have been secured with the exception of the determination of humus and nitrogen in the humus. In order for a method to be practical for industrial work it must be rapid as well as accurate. Time is a very important factor. Many samples of soils require several days' leaching to free them of calcium salts and several days more for the extraction of the humus.

About two years ago while working with one of these slowly leaching soils it was observed that the caustic potash solution of humus was strongly ammoniacal. A slightly ammoniacal solution is, of course, unavoidable, for caustic alkalies will liberate the ammonia present in the form of ammonium salts and also readily decompose some of the weaker compounds of amid nitrogen. But where the time of leaching extended over several days more ammonia was apparently liberated, than was originally present in the form of these easily decomposed salts. Other work prevented further investigation at that time, and the subject was not taken up again until this winter when the rush of soil samples to the laboratory almost compelled experimenting with humus with a view of finding a more rapid method. During these experiments some interesting results developed.

Several samples of soil, washed free of calcium salts with dilute hydrochloric acid, were leached with a 4 per cent. solution of caustic potash. In the course of a few hours, varying with the

richness of the sample in nitrogen, a piece of red litmus suspended in the mouth of the flask containing the leached solution would turn blue in ten or fifteen minutes. The same solutions, after standing twenty-four hours, would liberate enough ammonia to turn the litmus blue in about five minutes, and after standing several days the change of color was very quick. In several cases the ammonia could even be detected with the nose. From 5 to 10 grams of soil were used for leaching.

The above being true, it follows that the determination of nitrogen in the caustic potash extract is always too low by the amount of nitrogen lost in the form of ammonia. This loss apparently depends on the nature of the soil sample, the time occupied in leaching, and the care taken to prevent the ammonia escaping from the leaching apparatus. Therefore, since the nitrogen in the caustic potash extract is too low, it follows that the nitrogen in the humus would also be too low. This loss of ammonia doubtless partly explains the great liability of duplicate results of the determination of nitrogen in humus to disagree, and more particularly accounts for the variation in results by different analysts.

By Dr. Hilgard's method<sup>1</sup> humus is determined by evaporating the solution, leached from calcium-free soil with dilute ammonia, drying to constant weight, igniting, and weighing. The difference in weight is regarded as humus.

During the process of evaporation the ammoniacal humus solution undergoes digestion at the temperature of the water- or steam-bath. Either during this digestion or during the leaching process (probably during both), ammonia is absorbed from the leaching solution and enters into stable combination with the humus extract. The free ammonia is easily expelled by evaporation, but the humus residue left in the platinum dish after being dried at 100°, or even 110° C., retains part of the ammonia at least that it has taken into combination from the leaching solution. This added ammonia is easily expelled with lime or magnesia, but not all the nitrogen of the residue is thus driven off even with dilute caustic potash. The following analyses will illustrate this point:

<sup>1</sup> Wiley's "Agricultural Analysis," Vol. I, p. 324, § 311.



Total nitrogen in soil by direct determination. Gunning meth- od.	Humus.	Nitrogen in hu- mus extracted with caustic potash.	Nitrogen in hu- mus extracted with $\text{NH}_3$ eva- porated and dried at $100^\circ \text{C}$ .
Per cent.	Per cent.	Per cent.	Per cent.
0.159	1.860	0.67	0.97
0.097	0.775	4.39	9.39

was at first thought that the difference in the per cent. of nitrogen in the caustic potash extract and the ammonia extract presented the loss of nitrogen in the form of ammonia during extraction with caustic potash, but it was found that a similar difference existed when the utmost care was exercised to prevent the escape of ammonia from the caustic potash solution, during and after leaching.

These results led to the analysis of the soil residues which had been leached with caustic potash and those which had been leached with ammonia. *Approximately 50 per cent. of the total nitrogen originally present remained in the soil after leaching with caustic potash.*

Total nitrogen in soil.	Nitrogen left in soil after leaching with caustic potash.
Per cent.	Per cent.
0.159	0.097
0.132	0.066
0.097	0.038

The average of the second column of figures is very close to 50 per cent. of the first, or the total nitrogen in the soils. Present data is insufficient to determine whether this ratio is true for all soils taken from all parts of the state. The above samples and others showing similar agreement are mostly from the Santa Clara valley.

After leaching with ammonia and drying the soil residue at  $100^\circ \text{C}$ . or distilling the residue until the distillate was neutral to litmus paper, from a little over  $\frac{1}{2}$  to  $1\frac{1}{2}$  the amount of total nitrogen originally present in the soil was found in the residue. Results seemed to vary somewhat with the time occupied in extracting the free ammonia from the soil residue by heat, the

Ten grams of soil may be readily digested by this method.

distillation method giving slightly higher results than by drying at  $100^{\circ}\text{C}$ . This might have been expected since the conditions of the two processes are not exactly the same. One sample of Hawaiian soil containing 0.812 per cent. total nitrogen took up 0.430 per cent. of nitrogen from a 2 per cent. ammonia solution by digestion at the room temperature over night and retained it at  $100^{\circ}\text{C}$ . This gave a total nitrogen of 1.242 per cent.

These results seem to strongly indicate that the organic or mineral constituents of the soil left on the filter have the power to absorb ammonia from the leaching solution during the process of leaching to a far greater extent than has heretofore been supposed. It seemed highly probable that the soluble organic compounds in the extract, called humus extract, would also have this power of taking ammonia from the leaching solution. This point was demonstrated in the following manner: Five grams of soil, washed free of calcium salts, were distilled with lime and the nitrogen in the distillate determined. Then five grams of the same soil were extracted with ammonia after removing the calcium and magnesium salts according to Dr. Hilgard's method. The free ammonia was expelled from the extract by evaporating to dryness and the resulting residue distilled with lime and the nitrogen determined in the distillate. This was repeated with a number of samples and while the results seemed to vary considerably yet more nitrogen was invariably obtained from the ammonia extract distilled with lime, than from the soil distilled with lime. In the first case, that is where the soil was distilled with lime, it will be noted that the organic compounds which are insoluble in dilute caustic alkalies as well as the soluble ones were subjected to the action of lime in hot solution. Since lime will decompose some of these insoluble nitrogenous compounds it follows that more nitrogen should have been obtained in the first case than in the second had not the soluble organic compounds, leached from the soil, taken up nitrogen in the form of ammonia from the ammoniacal leaching solution. Hence, we conclude that Dr. Hilgard's method gives too high results for humus by the amount of ammonia taken up from the leaching solution and held in combination by the extracted organic matter.

Now, since nitrogen in the humus is determined by dividing the nitrogen in the caustic potash extract, which is too low, by

the humus, which is too high, the error would be multiplied and the result would be invariably too low. That this error is quite large and not to be neglected is clearly shown by the figures given above.

By a slight modification of the method the ammonia can be prevented from escaping during leaching with caustic potash. The following method seems to overcome all difficulties: The soil to be leached with caustic potash is placed in a funnel which is closed at the top with a stopper through which the leaching solution is admitted by a separatory funnel. The glass support of a Gooch crucible serves very well for the funnel holding the soil. The solution from the soil is run directly into dilute sulphuric acid, the bottle containing the same being sealed with a tube containing sulphuric acid. Gentle suction can be applied to this apparatus which greatly hastens the process without the least danger of losing ammonia.

It is more difficult to correct the second source of error; *i. e.*, the absorption of ammonia by the organic matter extracted from the soil. No very satisfactory results have been obtained although considerable time has been devoted to the matter.

Before leaching the soil for the extraction of the humus, it is washed with dilute hydrochloric acid until the filtrate shows no reaction for calcium. It is well known that the organic acids of soils form single and double salts with the alkali earths and with the oxides of some metals. Calcium is a stronger base than ammonia; therefore, an acid that would liberate calcium ought also to liberate ammonia from these double insoluble salts. We had supposed that this hydrochloric acid solution contained practically only the nitrates and nitrites present in the soil which would be worth considering only in exceptional cases.

Total nitrogen in soil.	Total nitrogen leached out with hydrochloric acid.	Nitrogen leached out with hydrochloric acid which is liberated with lime.
Per cent.	Per cent.	Per cent.
0.159	0.037	0.011
0.812	0.049	0.036

The above results show that it is not safe to assume the insol-

ility of organic matter and organic salts even in very dilute hydrochloric acid. We believe this also may be a source of no significant error in soil analysis.

It would be interesting to know whether the organic matter of soils of humid regions show the same tendency to absorb ammonia in such relatively large amounts as the soils that we have examined. This absorption of ammonia seems to take place at ordinary temperature as well as in hot solutions. The rate or maximum amount of absorption has not yet been determined. Hitherto we have regarded free ammonia as being excluded in the soil but it now seems highly probable that one of the functions of the organic matter of the soil is to absorb the free ammonia which comes to it in solution and that which is liberated in the soil itself. Possibly in nature occlusion precedes and directly aids absorption and combination.

Regarding the nature of humus little seems to be really known. Humus is regarded as the organic matter and mineral salts of organic acids extracted from soils by means of dilute alkalies. We have to deal undoubtedly with a highly complicated mixture of chemical substances in various stages of decomposition and combination. Many organic nitrogenous substances are soluble in dilute alkalies without having undergone a process of decomposition. This is true of the organic matter of plants as well as that of animals. Sun-dried grass, weeds, or wood, according to the generally accepted idea of the term, would not be regarded as humus. Yet, 27.30 per cent. of a sample of clover meal dissolved in 25 cc. of a 5 per cent. solution of ammonia at room temperature by standing over night. The undissolved portion contained 2.94 per cent. nitrogen. Providing this residue took up 1.5 per cent. free ammonia from the solution, which is doubtful, 35.76 per cent. of the total nitrogen of the clover meal was readily soluble and probably more would have been dissolved had the leaching process been used.

This is more or less true of other organic substances which find their way into soils and form a part of them. While clover meal may be an excellent fertilizer much of it would, nevertheless, have to be regarded as humus by the present methods of analysis. In fact in many respects clover meal extract acts as

humus is supposed to act. Part of it forms insoluble salts with calcium and is precipitated with alcohol.

If a soil be boiled with an excess of calcium or barium salts and the soil afterwards extracted with ammonia the filtrate will usually have a color closely matching that of dilute ferric chloride. If the same soil is then leached with hydrochloric acid and again leached with ammonia, the resulting solution will have a much darker color which is often almost black. Yet barium or calcium salts precipitate the organic matter in the caustic potash soil extract, leaving an almost colorless supernatant liquid. The precipitation is not quantitative.

Further experiments are already under way in the laboratory and we hope to have further data of interest in regard to humus and soil analyses in connection with field experiments with fertilizers.

CHEMICAL LABORATORY OF N. ORLANDT & CO.,  
April 2, 1900.

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## LECTURE EXPERIMENTS. REVERSIBLE CHEMICAL REACTIONS.

BY W. LASH MILLER AND F. B. KENRICK.

Received April 11, 1900.

LECTURES on physical chemistry are, at present, less in need of experimental illustration than those on any other branch of the science, being delivered, for the most part, to small classes of advanced students, who have ample opportunity for experimenting in the laboratory. Some of the conceptions and discoveries which form the subject-matter of that department have, however, proved of such importance, that it is very desirable to incorporate them into the elementary course. This has hitherto been rendered difficult by the lack of suitable lecture experiments.

Among the most important of these discoveries, is that of the *incompleteness* and *reversibility* of a very large number of chemical reactions. The application of thermodynamical methods in the treatment of such cases is an achievement of the present day, and necessarily forms one of the chief subjects of study of advanced classes. The "average student," however, whose practical acquaintance with chemistry is limited to a course in

analysis, knows nothing of all this. He knows the chemical reaction as a quantitative, non-reversible, and practically instantaneous phenomenon.

It does not occur to him that the reactions he meets with in the laboratory have all been selected because of these very properties, which render them convenient for the purposes of the analyst; generalizing from his one-sided experience, he is apt, half unconsciously, to form views on chemical affinity practically identical with those of Bergmann. Theories based on the rate of inversion of cane-sugar, and on Berthelot's experiments with alcohol and acetic acid—the experiments themselves are, unfortunately, quite unsuited to the lecture table—do not make much impression on one whose daily experience points in the other direction; if anything, they serve only to accentuate the feeling of unreality associated with the "other world" of organic chemistry.

Reactions involving the addition and removal of water of crystallization, or the formation and decomposition of double salts or other "molecular" compounds are likewise unsatisfactory. To be convinced, the student must see a "genuine" chemical reaction, *i. e.*, one used in analysis or on the large scale in chemical manufacture, reversed before his eyes.

The following half dozen reactions have been selected from this point of view; the instructions include all the details that we have found necessary in exhibiting them before a large audience.

#### I. AMMONIUM THIOCYANATE AND FERRIC CHLORIDE.

Approximately equivalent solutions of these substances are prepared, the first containing:

Ammonium thiocyanate.....	7.5 grams
Water .....	to make 200 cc.

and the second:

Commercial (basic) ferric chloride .....	6 grams
Concentrated hydrochloric acid (sp. gr. 1.175)....	25 cc.
Water .....	to make 200 cc.

Five cc. of each are mixed in a large beaker, about two liters of (tap) water added, and the orange-colored mixture poured in equal quantities into four beakers.

	Is added	The color becomes	Reaction.
t	5 cc. am. thiocyanate solution.	dark red	→
nd	5 cc. ferric chloride solution.	dark red	→
d	50 cc. saturated am. chlor. sol.	almost colorless	←
ile	the fourth is kept for comparison.	orange	

the reaction be represented by the equation



the amount of ferric thiocyanate be judged from the depth of the color of the solution, the reaction between equivalent quantities must be regarded as incomplete. The changes of color interpreted by the arrows in the last column (indicating the direction of the reaction).

In order to show the effect of dilution in destroying the ferric thiocyanate (dissociation), equal quantities of the orange-red mixture may be placed in two rectangular glass troughs of equal width, one of which is about twice as thick (from back to front) as the other. Water is then added to the solution in the larger trough until the level is the same in both, and a piece of white paper held at a little distance behind the two troughs. From the front, the more dilute solution appears much less deeply colored than the other. For purposes of comparison, potassium permanganate may be used, which gives the same color in the two vessels. Rectangular battery jars answer well, as the change in color is so marked that unevenness of the glass is of no moment.

## II. BISMUTH CHLORIDE AND WATER.

"bismuth solution" is prepared as follows:

Commercial "bismuth trinitrite" ..... 40 grams  
 Hydrochloric acid (sp. gr. 1.175) ..... 40 cc.  
 Mix together in a mortar, as the powder cakes; a trifling residue may be filtered off.

The reaction with water is represented by the equation:



To	50 cc. water	add 5 cc. bismuth solution	→
Add	5 cc. hydrochloric acid (sp. gr. 1.175)		←
"	75 "	water	→
"	5 "	acid	←
"	200 "	water	→
"	10 "	acid	←
"	500 "	water	→
Pour in	acid from the reagent bottle		←

The reaction may be carried out in a glass cylinder, about three inches in diameter, holding about a liter. If small marks be made at the proper heights on the cylinder the water may be poured in without measuring.



The acid may be delivered from a pipette or burette, or it may be dipped out of a beaker with the little measure figured in the margin (made of a piece of test-tube and a glass rod).

### III. AMMONIA WITH SALTS OF COPPER AND OF SILVER.

*Silver Bromide.*—Excess of potassium bromide is added to 15 cc. of fifth-normal silver nitrate solution; the precipitate is washed once by decantation, shaken with 15 cc. of ammonia (sp. gr. 0.915) and filtered. In the solution so obtained a precipitate is produced,

- (a) adding a drop of potassium bromide solution,
- (b) adding a drop of silver nitrate solution,
- (c) adding five times its volume of water,
- (d) boiling, or
- (e) exposing (in a fractionating flask) to the vacuum of a filter-pump.

*Copper Sulphate.*—Five cc. copper sulphate solution (100 grams blue vitriol in 1 liter) are mixed with 5 cc. 5/1 normal ammonia and diluted with 400 cc. *distilled* water. The addition of 400 cc. more distilled water produces a precipitate. If the reaction be carried out in a flat glass cell (an inch thick) with an incandescent lamp behind it, the change from clear to turbid is very distinct. This experiment should be rehearsed immediately before the lecture, as the presence of traces of acid, carbon dioxide, or ammonia salts, largely increases the amount of water necessary to produce a precipitate. If tap water be used instead of distilled water, half as much again may be required.

### IV. FORMATION AND DISSOCIATION OF WATER, ETC.

*Eudiometer.*—A very convenient lecture table eudiometer con-



of a straight glass tube (10 mm. diameter and 100 mm. long) open at one end and fused to a capillary with capillary tap at the other. The platinum wires are sealed through the wide tube just below the junction with the capillary, and the divisions are marked with rings of Brunswick black. A piece of iron pipe, widened at the mouth, serves as a mercury trough.

Measured volumes of the various gases ( $H_2$ ,  $O_2$ ,  $Cl_2$ , etc.) may be admitted through the tap, if the eudiometer be first filled with mercury, and the division corresponding to the volume desired be level with the surface of the mercury in the iron

trough. The union of two volumes of carbon monoxide and one of oxygen may be shown by introducing the 30 per cent. potash above the mercury in the eudiometer; while in a subsequent experiment (without potash) the volume of the carbon dioxide formed may be determined.

The formation of hydrochloric acid from one volume of hydrogen and one of chlorine may be shown to a fair degree of accuracy, if the mercury trough be replaced by brine from the chlorine gasometer in a tall glass cylinder.

In many cases, notably with  $CO$  and  $O_2$ , the gases must be shaken by shaking the tube vertically before passing the spark, or explosion will occur.

*Deville's Tube* (Fig. 3).—A coil of platinum wire hung vertically in the neck of a fractionating flask and heated by electricity is just as efficient as any other "white hot platinum tube" for bringing about the dissociation of water vapor. It works very much better than the noisy induction sparks commonly employed. Concentrated ammonia (sp. gr. 0.880) be warmed in the flask, the apparatus may be made use of to effect the decomposition of  $NH_3$  into  $N_2$  and  $H_2$ .

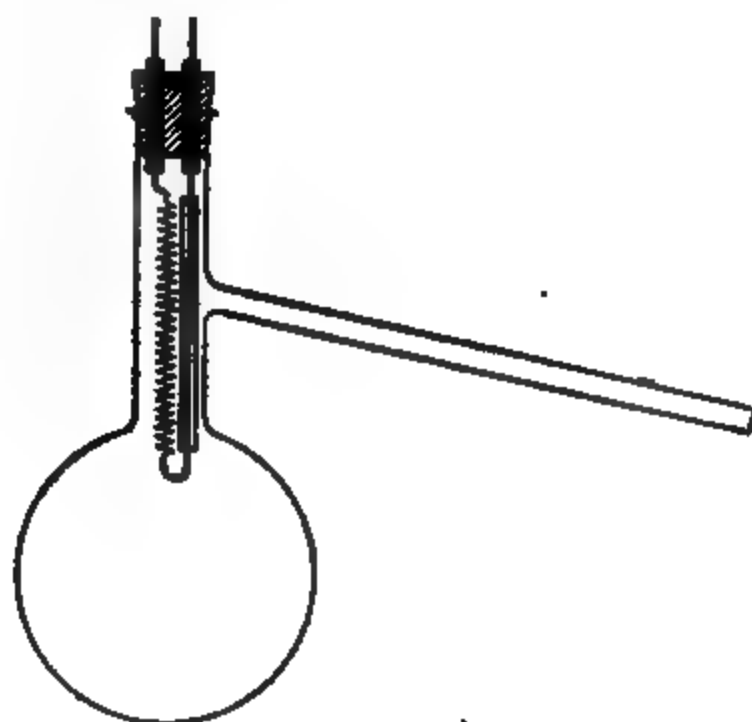


Fig. 2

#### V. SULPHURIC ACID AND SODIUM CHLORIDE.

Concentrated sulphuric acid is poured into its own volume

of a saturated solution of common salt in a test-tube. The mixture may be cooled under the tap and shaken; but in general



*Fig. 3.*

crystal of Glauber's salt must be added before crystallization will occur. The liquid is poured off, and the crystals dried on a piece of unglazed porcelain.

2. If some of the sodium sulphate so prepared be covered with concentrated hydrochloric acid (on a watch-glass) it is at once changed to a fine powder of sodium chloride; which, in turn, may be freed from acid on a porous plate.

To demonstrate the change from chloride to sulphate, and back again, mix a drop of the original salt solution with a little water on a piece of glass the size of an ordinary lantern slide, warm till crystallization sets in, and throw the image on the screen (Fig. 4). The same may be done with small portions of the sulphate (Fig. 5) and sodium chloride formed in the experiment.

#### VI. ANTIMONY CHLORIDE AND HYDROGEN SULPHIDE.

An antimony solution is prepared as follows: Dissolve 2 grains of tartar emetic in 15 cc. hydrochloric acid (sp. gr. 1.175); the

35 cc. water. (This solution cannot be kept more than two or three hours as a precipitate of oxychloride is slowly formed.)



- (a) Pass a little  $\text{H}_2\text{S}$  into 5 cc. antimony solution.....  $\rightarrow$
- (b) Add 8 cc. hydrochloric acid (sp. gr. 1.175) .....  $\leftarrow$
- (c) " 5 " antimony solution.....  $\rightarrow$
- (d) Heat, not to boiling.....  $\rightarrow$
- (e) Cool again (in a dish of water) .....  $\rightarrow$
- (f) Add 6 cc. hydrochloric acid.....  $\leftarrow$
- (g) Pass in  $\text{H}_2\text{S}$  under pressure of 3 meters Hg.....  $\rightarrow$
- (h) Reduce pressure by filter-pump .....  $\leftarrow$

Notes.—(c) If the addition of antimony does not bring down

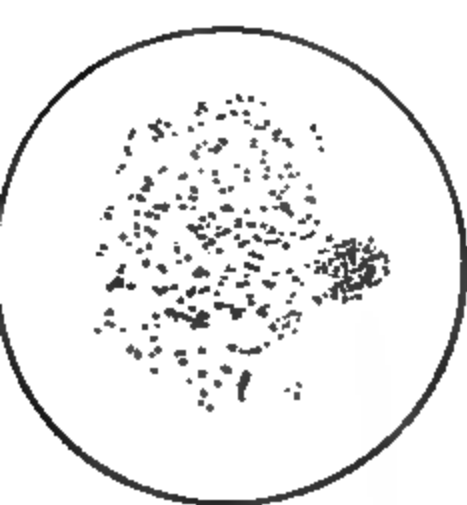


Fig. 4.

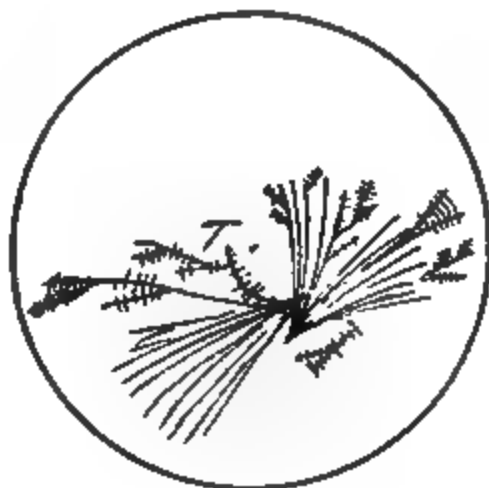


Fig. 5.

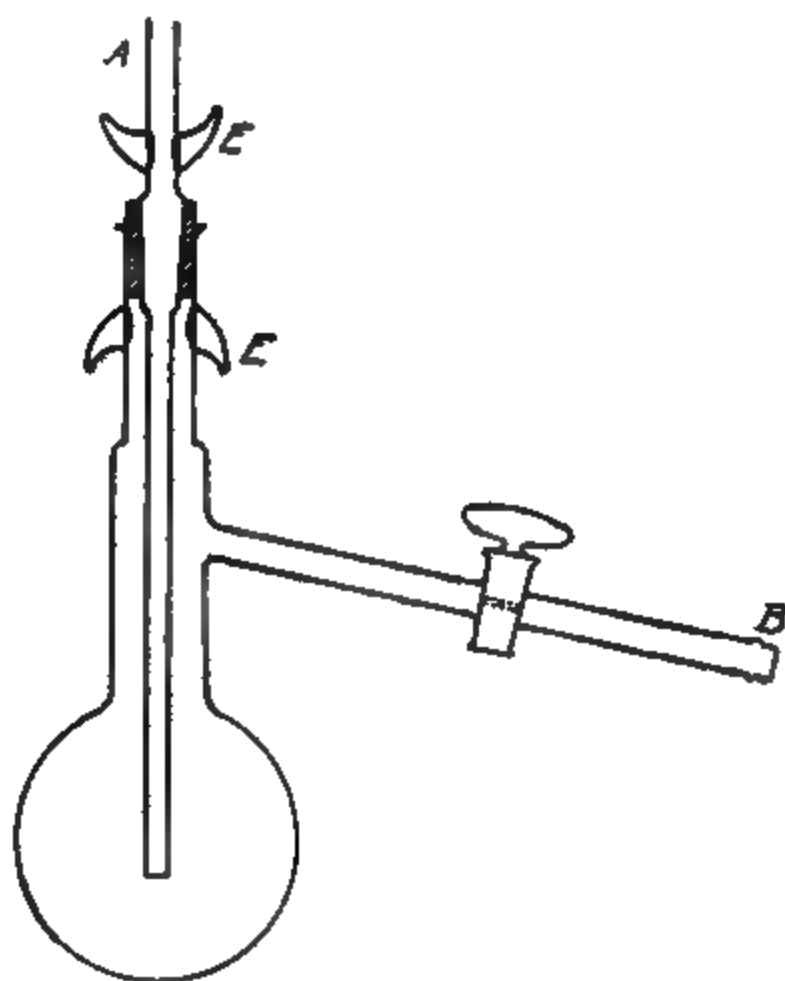
ly heavy precipitate, hydrogen sulphide should be passed again, or there will be no precipitate in (e).

Cool only until a precipitate appears, then add the acid (f) finish[cooling]; if too much precipitate is formed it dissolves slowly in the acid.

The necessary pressure may be secured by means of the described below. With a rubber "syringe" (bulb and valves) worked by hand, a pressure of about one meter of mercury (above the atmosphere) may be maintained; this is sufficient for the purposes of the experiment, but the precipitate is much more slowly than when the pump is used. The effect of the vacuum (h) also is to save time.

The reaction may be conveniently carried out in the glass ves-

sel represented in Fig. 6. The hydrogen sulphide enters by *A* which may be tied in by wire round the ears *E*. *A* is connected to the pump by rubber pressure tubing, and *B* (the outlet) to



*Fig. 6.*

the flue. All taps should be wired in. Joints may be made with ordinary rubber tubing covered with cloth and wired.

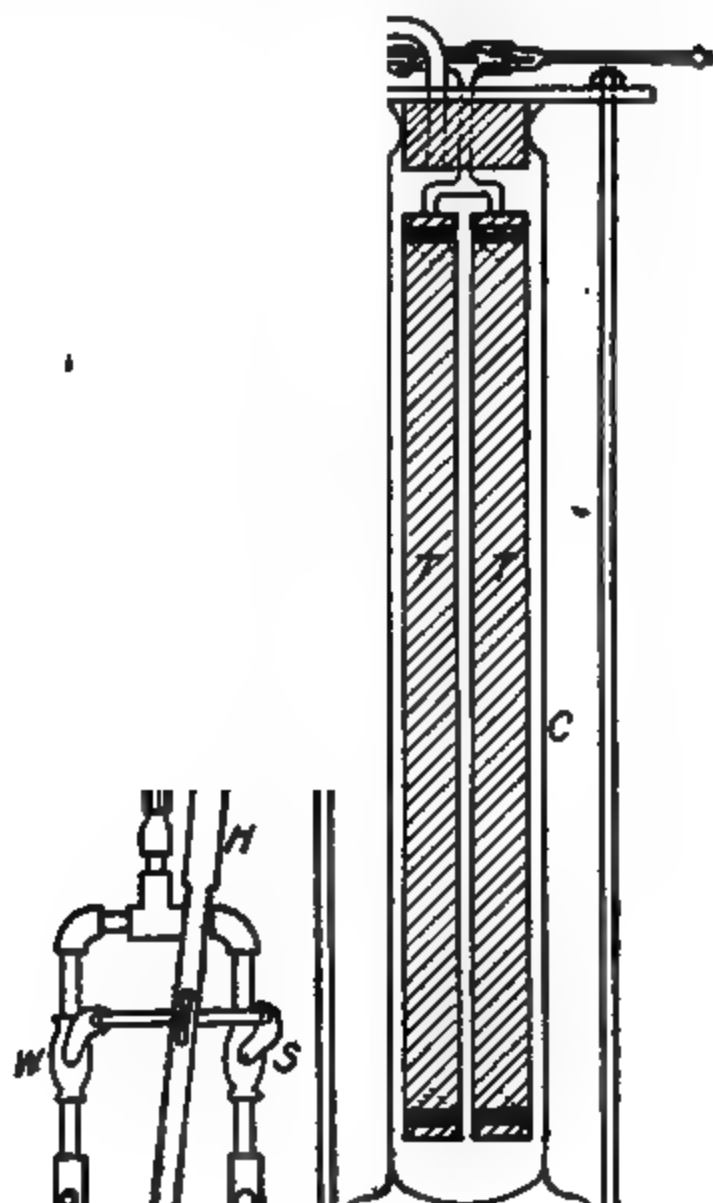
#### VII. PRESSURE PUMP FOR GASES.

The accompanying figure (Fig. 7<sup>1</sup>) represents the pump referred to in the preceding paragraphs. It consists of three pieces of black rubber tubing T (of which two are shown in the figure) each 1 inch in diameter and 18 inches long, closed at the bottom and connected at the top by glass tubing to a pair of Bunsen valves. The valves are shown separately in Fig. 8 and are so arranged that on compressing the tubes the gas contained in

<sup>1</sup> For the sake of clearness, the taps and handle which are actually behind the cylinder, are represented to one side of it.

m is forced out through D, and on removing the pressure are refilled through F.

The compression is effected by moving the handle *H* to the position indicated in the figure, thereby opening the brass tap (communicating with the water mains) and closing *S* (to the tank). Water thereupon flows through the glass pipe *P* into the



*Fig. 2.*

glass cylinder *C* containing the rubber tubes *T*. Moving the handle in the opposite direction fills the tubes again with gas. The top of the cylinder is closed by a rubber plug covered with a brass plate ( $\frac{1}{4}$  inch thick) which is held down by four  $\frac{1}{4}$ -in

brass rods threaded at the ends and provided with nuts. The ends of the tubes are closed by glass plugs, wired in ; in order to keep the rubber from tearing, a wedge-shaped piece of cork is inserted at each end, as shown by the dotted lines in the figure.

The capacity of the pump is 500 cc. Three strokes are suffi-

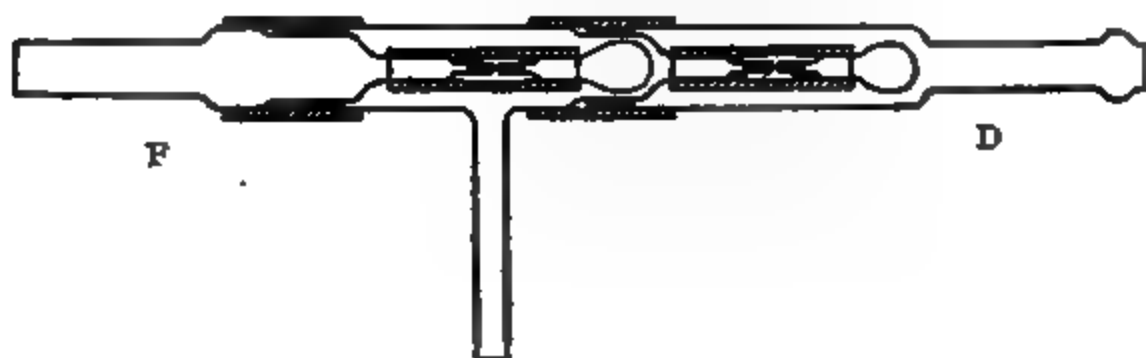


Fig. 8.

cient to attain the maximum pressure in the antimony sulphide experiment.

With this apparatus a gas can be brought to the pressure of the water system *without coming into contact with any liquid*. Higher pressure may be attained by using a force pump ; the limit depends only on the strength of the apparatus and on the ratio between the variable volume (rubber tubing) and the constant volume (glass tubing) between the valves.

THE CHEMICAL LABORATORY OF THE UNIVERSITY  
OF TORONTO, April, 1900.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA  
UNIVERSITY, No. 23.]

### A NEW ELECTROLYTIC CELL FOR RECTIFYING ALTERNATING CURRENTS.

BY W. L. HILDBURGH.

Received April 9, 1900.

**I**N electrical work an automatic device which will permit a current to pass through it in one direction only is frequently desirable, for rectifying alternating currents, for example, or for preventing a back-flow of current due to polarization. In addition to mechanical commutators several arrangements for the purpose have been previously known, but, with one exception, they are applicable to comparatively high voltages only. This exception is the two-cell rectifier described by Prof. M. I. Pupin

the American Physical Society.' In the present paper a class of electrolytic cells capable of affecting currents of very low voltage is described. These cells act by the production of a counter E. M. F. of polarization whose intensity depends on the direction of the E. M. F. impressed, and have been termed "Single Cell Rectifiers."

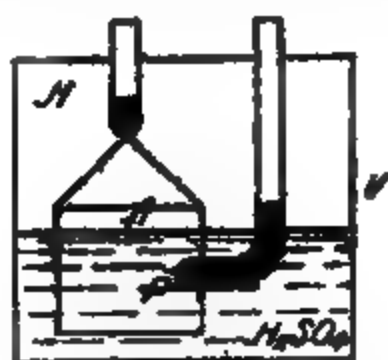
If a plate of copper be placed in dilute sulphuric acid it will dissolve. If, however, a platinum electrode be placed in the acid, and the copper made the anode, a very small E. M. F. is sufficient to cause the copper to dissolve freely and hydrogen to be deposited on the platinum, and a current will pass until all the copper is carried into solution. When the source of the E. M. F. is reversed a momentary current flows, the platinum plate becomes covered with oxygen, and, if the impressed voltage is not too high, the current ceases almost completely. That is, the cell  $\text{Cu} | \text{H}_2\text{SO}_4 | \text{Pt}$ , producing no net effect, permits the passage of continuous currents of low E. M. F. through it in one direction only.

By placing a number of such cells in series it is possible to regulate the flow of a current of any voltage whatsoever. Such a device may be used for the rectification of alternating currents by regulating the size of the platinum plate that the quantity of current necessary to polarize it as anode is less than that which is required during the next half-wave, when the platinum acts as cathode. The smaller the platinum, or passive plate, the higher the degree of rectification (asymmetrical efficiency) attainable. The amount of rectification is dependent, however, not only on the size of the passive plate, but also on the quantity of current which can pass; that is, on the *current density* at the surface of the plate. Consequently the lower the resistance in the circuit the lower the frequency of the alternating E. M. F. impressed the greater will be the asymmetrical efficiency.

In the cell  $\text{Cu} | \text{H}_2\text{SO}_4 | \text{Pt}$ , or more properly speaking,  $\text{CuSO}_4 | \text{H}_2\text{SO}_4 | \text{Pt}$ , considerably more energy is required to produce hydrogen at the passive plate than is given out by the solution of the copper, or active plate. As this evidently lowers the efficiency of the device by producing an E. M. F.

counter to the main flow of current, means should be adopted of making the energy given out at the active plate and that absorbed at the passive as nearly equal as possible. By making the active plate of the substance given off at the passive plate by the current in the "useful" direction this condition can be nearly fulfilled. The substance produced at the passive plate should be a gas, as otherwise that electrode will soon become covered with a layer of active substance and cease to be inert. Gaseous active electrodes may be formed with hydrogen, oxygen, chlorine, etc., as the active material, absorbed by platinum or in chemical combination with some metal.

Of such electrodes the writer has found that hydrogen when absorbed by platinum black gives by far the best results, and can be made, in addition, self-regenerating, giving a "continuous-acting" rectifier such as is shown in illustration. V is a sealed vessel into which pass two mercury-contact electrodes A and P. A, the active plate, is of platinized platinum, partly in hydrogen



gas (H) and partly in sulphuric acid ( $H_2SO_4$ ). P, the passive electrode, is a platinum wire sealed into glass and cut off to give the desired surface of contact with the liquid, or filed plane with the sealed end of the tube. The "useless" current carries oxygen to P, but is of insufficient voltage to produce bubbles, and the cell polarizes. In the opposite, or "useful" direction hydrogen is carried from A to P, is there given off in bubbles, and goes back to join again the gas H. It is clear that since nothing but hydrogen is produced at P, provided the impressed E. M. F. is not too high, that the cell will work for an indefinite time, or until changes in the surface of the platinum electrodes stop the actions described.

For the most perfect action of rectifiers of this class there



ould be no counter E. M. F. in the "useful" direction. In the hydrogen-cell it requires from a few thousandths of a volt to 0.085 volt to carry the gas through the electrolyte, the pressure varying with the size of the passive electrode and the condition of its surface, the concentration of the liquid, the temperature, etc. This counter E. M. F. can be "balanced," as is necessary for certain kinds of work, by adding an E. M. F. in the "useful" direction, taken from a slide-wire in series with 1 or 2 cells in a battery.

It is impossible to specify the size of the various parts of a cell without knowing all the conditions under which it is to be used. As a general rule the small (passive) electrode should be of the dimensions of a millimeter, ranging in area from a small fraction of 1 sq. mm. up to 100 sq. mm., according to the frequency and the resistance or inductance in the external circuit. The platinized electrode should be of sufficient size to absorb hydrogen as fast as it is given off at the passive plate. For the electrolyte part sulphuric acid to about 8 or 10 of distilled water, from which the oxygen has been removed by boiling or exhaustion, serves very well. The vessel need only be large enough to contain the two electrodes and a little liquid and gas, the latter two being employed continuously, and only a very small quantity being in the cell at any one time. The larger electrode should be thoroughly washed after platinizing, as otherwise platinum may be carried over to the smaller electrode, impairing the efficiency. A jar of water, in which the cell may be kept, offers a convenient method of sealing, for laboratory use.

The following points will be found of service in working with the cell, and have been obtained, for the most part, by the study of curves taken with alternating currents. More complete discussions of the theory and actions of rectifiers of this class will be found in other papers by the writer.<sup>1</sup>

The smaller the plates the greater the asymmetrical efficiency. The greater the resistance in the circuit the less the asymmetrical efficiency.

The higher the frequency the less the asymmetrical efficiency. The higher the frequency, or the greater the resistance, or the larger the plates, the higher may be the impressed alternating

<sup>1</sup> *Elec. World and Eng.*, 1900; *School of Mines Quarterly*, July and Oct., 1900.

E. M. F. in a given cell, without producing oxygen bubbles on the smaller plates.

In a perfectly "balanced" rectifier, as long as the impressed E. M. F. is not too high, the quantity of current capable of doing unidirectional work is proportional to the impressed E. M. F.

If the active E. M. F. of a rectifier be too high a continuous current will flow, and the amount of rectification be dependent on the impressed E. M. F.; if the latter be low, rectification may cease completely.

If the active E. M. F. be too low the amount of rectification is dependent on the impressed E. M. F., and may become zero if the latter be low. This property prevents the use of rectifiers in circuits in which any considerable counter E. M. F. is produced.

Rectifiers for high E. M. F. can be formed by joining a number of cells in series. The passive plates in each can then be correspondingly increased in size, while the whole set gives the same efficiency as one of the cells gave before its electrode was enlarged. The number of rectifiers and the impressed E. M. F. should be proportioned to their circuit exactly as primary cells are proportioned, each primary cell being represented by a rectifier and a certain portion of the impressed E. M. F.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 24.]

## A METHOD FOR THE DETERMINATION OF ELECTRICAL CONDUCTIVITY WITH DIRECT CURRENT INSTRUMENTS.

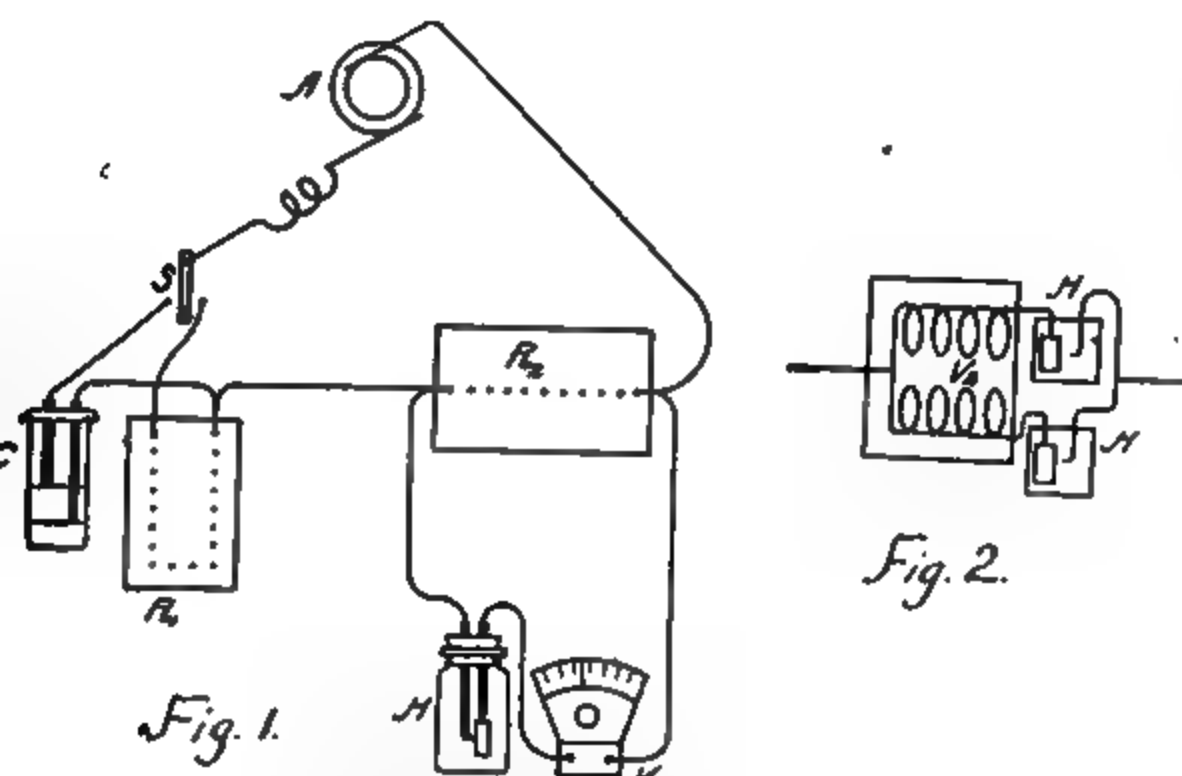
BY J. LIVINGSTON R. MORGAN AND W. L. HILDBURGH.

Received April 3, 1900.

**I**N the determination of electrical conductivity, in order to prevent errors, it is necessary to use an alternating current whose frequency is of such a value that the electrodes, during a half period of the alternating current, receive a polarization which is negligible compared to the voltage impressed. Up to the present time it has been difficult to detect small quantities of an alternating current, except by aid of the telephone. In the

Kohlrausch-Ostwald method the electrolyte is placed in one arm of a Wheatstone bridge, an alternating current passed through it and the resistance balanced on the bridge wire against a known value by aid of the telephone. McIlhiney<sup>1</sup> passes a direct current through a direct current measuring instrument and then transforms it into an alternating current with a rotating pole changer and carries it through the electrolyte.

One of us<sup>2</sup> has designed a number of rectifying cells for the purpose of permitting the passage of current in one direction only, so that an alternating current in going through them is more or less rectified and has many of the properties of a direct current. Of these cells the most suitable for laboratory use is the continuous acting hydrogen cell, which has been applied to conductivity measurements in the following way: The apparatus for the substitution method is arranged as in Fig. 1. The alter



A is the source of the alternating current, S a switch allowing either C or  $R_1$  to be in the circuit, C is the unknown resistance,  $R_1$  and  $R_2$  resistance boxes, H the hydrogen cell rectifier, and V the voltmeter or galvanometer.

Alternating current from A passes through the electrolyte in C and the non-inductive resistance  $R_1$ , to the terminals of which is connected a direct current instrument in series with the rectifying

<sup>1</sup> This Journal, 20, 206 (1898)

<sup>2</sup> W. L. Hildburgh: This Journal. Also Ph.D. thesis in press and School of Mines Quarterly, July and October, 1900. Also Elec. World and Eng., 1900.

cell. The reading of the instrument is noted when the current passes through the unknown resistance  $C$ , then  $S$  is moved so as to replace  $C$  by  $R_1$ , a non-inductive adjustable resistance, and this varied until the same reading is observed as before. If the proper precautions have been observed, the resistance of  $R_1$  is equal to  $C$  and the conductivity may be calculated.

For the source of the alternating current we have found a small alternator to be more satisfactory than the small induction coils commonly used; there is, however, apparently no reason why a properly arranged coil should not be available. With the ordinary (Kohlrausch) electrodes and an alternating pressure of 2 volts the results were found to agree very satisfactorily with those obtained by the Kohlrausch-Ostwald method.

For the highest sensitiveness the following conditions should obtain. The resistance of  $R_1$  which must be small compared with  $C$ , should be as large as possible.

The instrument  $V$  (galvanometer) should give large readings with small currents, and its resistance should be low. The frequency of the alternating current should be as low as allowable, the voltage as high as allowable, and the electrodes in  $C$  large. The area of the inert electrode in the rectifier should be small so as to give a high asymmetrical efficiency (percentage of rectification).

A considerably more sensitive arrangement is obtained by replacing  $R_1$ ,  $H$  and  $V$  by a differential wound instrument whose two windings are exactly alike and are in series each with a rectifier. If these two coils are properly arranged all waves of one sign will go through one winding, and all of those of the opposite sign through the other (Fig. 2). This utilizes the whole of both half waves of current, instead of only a part of one, so that the deflection of the needle is very much greater.

The hydrogen cell rectifier can be "balanced" by adding a small electromotive force in series, so that up to a certain point a direct current instrument in series with it will give readings almost exactly proportional to the alternating current. Knowing the alternating voltage, the rectification constant of the hydrogen cell and the resistances of  $C$  and  $H$ , the resistance of  $C$  can be calculated directly from the readings of  $V$ . This method can be used without "balancing" the cell by calibrating  $V$ , using

rent known resistances in place of C. The resistance of C then be read directly from the scale of the instrument. In these modifications the frequency of the alternating current remain the same, and neither is as accurate as the first one substitution.

The hydrogen cell rectifier permits the use of an optical detector instead of the telephone in the Kohlrausch-Ostwald method. The telephone is replaced by a resistance and a sensitive galvanometer in series with the "balanced" cell, arranged like G and H in Fig. 2. The point on the slide wire which gives no deflection is then the same one as found by the telephone.

In "balance" the cell the circuit of a Leclanché is closed through a high resistance and a slide wire. The alternating current being stopped, an electromotive force is taken from the slide wire and sent through the rectifier, the slide being left just beyond the point which shows deflection. If "overbalanced" the cell will give a constant deflection, but if "underbalanced" the low voltage current obtained will give no deflection. An arrangement like Fig. 2 will give here greater sensitiveness, but the method of substitution as first described is the simplest and gives the best results.

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CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, UNIVERSITY OF MICHIGAN.]

## ON THE PREPARATION OF POTASSIUM XANTHATE FOR NICKEL DETERMINATIONS.

BY E. D. CAMPBELL.

Received April 23, 1900.

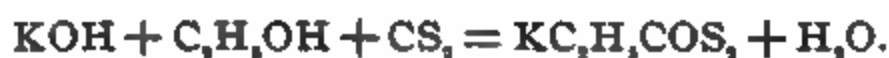
In 1895 the author with W. H. Andrews published a method for the determination of nickel in nickel steel.<sup>1</sup> This method has been in use in this laboratory since its publication and has given very satisfactory results, provided the potassium xanthate had been properly prepared. The potassium xanthate usually found on the market has not been satisfactory owing to the fact that the salt after making has not been carefully washed and dried. The practice in this laboratory has been to have each student prepare the potassium xanthate used in his own work.

<sup>1</sup>This Journal, 17, 125.

The method of preparation is as follows: A weighed amount of fused potassium hydroxide is placed with absolute alcohol in a tightly stoppered flask and digested cold, with occasional shaking, until solution is complete, except for the small amount of potassium carbonate usually present; 2.5 cc. of absolute alcohol should be used for each gram of potassium hydroxide.

The clear solution of potassium hydroxide is poured off from any undissolved carbonate into a beaker and cooled by standing in ice-water. Pure carbon disulphide is now gradually added with constant stirring until 1 cc. has been added for each gram of potassium hydroxide used. When all the carbon disulphide has been added the stirring is continued, the beaker being kept in ice-water until the temperature is reduced to 10° C. or below.

The formation of potassium xanthate takes place according to the reaction:



The precipitated salt is transferred best to a Buchner funnel in which a filter-paper has been laid, and the solution drawn off by means of a pump. When the solution has been drawn off through, the precipitate is pressed rather firmly down in the funnel and washed once by pouring over it just enough absolute alcohol to cover it well. When the alcohol has been drawn off through, the precipitate is washed twice in a similar manner with ether. The washed xanthate thus prepared is thoroughly dried at about 100° C. and after pulverizing is ready for use.

We have found that potassium xanthate made by the above method is perfectly stable, just as accurate results having been obtained with xanthate that had been kept three years as with the fresh material. With ordinary care in preparation, the yield of potassium xanthate is about 10 per cent. greater than the amount of potassium hydroxide used.

ANN ARBOR, MICH.,  
April 16, 1900.

# THE JOURNAL

OF THE

# AMERICAN CHEMICAL SOCIETY.

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## ON THE RELATION OF THE REDUCING POWER OF NORMAL URINE TO THE AMOUNT OF CERTAIN NITROGEN COMPOUNDS PRESENT.

By J. H. LONG.

Received April 27, 1900.

THE reducing power of normal urine is easily observed by the application of certain reagents and was at one time supposed to be largely or mainly due to the presence of dextrose or some similar body. In fact, based on the reducing power alone, estimates of the amount of carbohydrates in urine were frequently made and are still occasionally found in the text-books of urine analysis and physiological chemistry. Later, doubt was thrown on this conclusion and the presence of even traces of sugar in normal urine was disputed. Seegen<sup>1</sup> made many experiments in this direction and came to the conclusion that if any sugar at all is present it cannot be in amount above 0.006 per cent. The same result essentially was reached by several others, but in most cases the methods of examination employed were open to criticism as they did not provide for the actual separation and identification of a sugar, supposing it present.

Meanwhile E. Fischer<sup>2</sup> proposed the reaction for the separation of sugars by the phenylhydrazine test, and von Jaksch<sup>3</sup> and

<sup>1</sup> *Ztschr. physiol. Chem.*, 9, 332.

<sup>2</sup> *Ber. d. chem. Ges.*, 17, 579 and 20, 82.

<sup>3</sup> *Ztschr. anal. Chem.*, 24, 478.

thers applied it to the identification of sugar in urine. Bau-  
ann<sup>1</sup> showed the ready production of benzoic esters of dextrose  
and this general method was soon applied in urine examination  
by Wedenski,<sup>2</sup> Roos,<sup>3</sup> Salkowski,<sup>4</sup> and others. The amount of  
the pentabenzonic ester found in this way was quite variable but  
always small. In Salkowski's test the range was from 1.22  
grams to 3.36 grams in 1000 cc. of urine representing the whole  
day's excretion. In Wedenski's experiments the maximum  
amount was ten times the minimum found. Later Baisch made  
two important contributions on the subject of the nature and  
amount of the carbohydrates in the urine<sup>5</sup> and places the content  
of these bodies somewhat higher than Seegen, but still very low.  
His results give the average excretion of reducing carbohydrates  
as 0.100 gram to the liter. About the same time Allen published  
an interesting paper on the subject<sup>6</sup> and reached nearly the  
same result.

It is quite evident from the foregoing that while the existence  
of sugar in the urine may be looked upon as settled, the amount  
is very small and far from accounting for the total reduction.  
This has been reported by some authors as corresponding to 0.15  
per cent. of dextrose while others place it as high as 0.4 per  
cent., in the mean.

#### NATURE OF THE REDUCING BODIES.

When speaking of reduction the behavior toward some metal-  
lic solution, generally toward copper oxide, is usually in mind.  
Among substances, other than sugar, which occur normally in  
urine the most important from the standpoint of this behavior  
are doubtless uric acid and creatinin. Glycuronic acid is often  
referred to as having an important action here, but the amount  
ordinarily present is too small to be practically considered in  
comparison with the others. The reducing power of uric acid  
has been long known and under certain definite conditions an  
equation may be written expressing the amount of oxygen  
absorbed in passing into several related bodies. The reducing

<sup>1</sup> *Ber. d. chem. Ges.*, 19, 3218.

<sup>2</sup> *Ztschr. physiol. Chem.*, 13, 122.

<sup>3</sup> *Ibid.*, 15, 513.

<sup>4</sup> *Ibid.*, 17, 229.

<sup>5</sup> *Ibid.*, 18, 193 and 19, 339.

<sup>6</sup> *Analyst*, 19, 178.



of creatinin is fully as important as is that of uric acid, besides it is more readily followed and measured. It occurred to me, therefore, that some light could be thrown upon the question of what part a sugar plays in the total reduction by determining as accurately as possible in a large number of normal urines the amount of uric acid and creatinin present, and subtracting then the reducing power of these from their relations to an oxidizing solution previously determined. The difference between the total reduction and that due to these bodies would then measure the reducing power of the sugar present, provided no other substance has been overlooked which exhibits reducing action. The possibility of the existence of such a substance or substances in the urine must, of course, be conceded, especially since the ratio of carbon to nitrogen present, as found by direct analysis, is much higher than that calculated from the amount of the determinable constituents present. The new substance recently separated from urine and called oxyproteic acid by Bondzynski and Gottlieb<sup>1</sup> is supposed by Pregl<sup>2</sup> to account for this ratio, and to be, after urea, the most important body in urine. The analyses made by Pregl show it to contain 30 per cent. of carbon and 8 per cent. of nitrogen, and to amount to 6 or 8 grams daily. He states, however, that the product, as separated by his methods of precipitation and filtration, is quite devoid of any reducing action on alkaline solutions. Toepfer has also recognized this peculiar uric acid<sup>3</sup> but claims that the amount found by Bondzynski and Gottlieb is too high, because the barium salt separated is always contaminated by the presence of much coprecipitated matter. It is certainly remarkable that an acid as abundant as this is supposed to be should have so long escaped detection, and this fact suggests caution in generalizing too much from the results of urine analyses, however carefully they may be made; but up to the present time no substances have been found in the urine in sufficient quantity to account for the reducing power save those mentioned, and it is from this, as a working basis, that the following investigation was undertaken.

While many substances have been employed as reagents in

<sup>1</sup> *Centralblatt für Physiologie*, 11, 648.

<sup>2</sup> *Bücher's Arch*, 75, 87, 1899.

<sup>3</sup> *Centralblatt für Physiologie*, 11, 830.

this reduction test some form of copper solution has usually been found practically the most useful. A weak solution of methylene blue is reduced readily by sugar and creatinin in alkaline solution, and very slowly by uric acid, but as the reduced product is oxidized with extreme readiness in contact with air, with return of the blue color, the reagent is not suitable for quantitative measurements. A weak solution of safranine is also reduced by sugar in alkaline medium and apparently not at all by uric acid or creatinin, but the amount of sugar necessary to produce an appreciable effect is greater than that usually found in normal urine, so that this reagent is not practically available. Measurement of reduction by aid of bismuth or mercury salts is also possible, but, as is well known, the methods are lacking in delicacy.

Among the various copper solutions used in sugar analysis there are several which may be employed with very weak solutions corresponding to normal urine. The best of these appear to be some form of the ammonia-copper solution recommended by Dr. Pavy. This was first made by diluting 120 cc. of Fehling's solution with 300 cc. of strong ammonia and water enough to make 1 liter. Pavy assumed that each cubic centimeter of this solution oxidizes 0.5 mg. of dextrose, and has, therefore, one-tenth the strength of the ordinary Fehling solution, which is approximately true. Several modifications of the solution have been proposed with variations in the amounts of copper sulphate, ammonia, and fixed alkali. Finally, the Loewe solution containing glycerol has been made the basis of the dilution, instead of the Fehling solution containing a tartrate; the Purdy solution is made in this way.

As the oxidizing power of the solution changes with these variations, it is important to recognize the extent of this alteration and allow for it if necessary. The composition of several of the best known of the modifications is here given, the original Pavy solution being added for comparison. The volume is one liter in each case.

	Copper sulphate. Grams.	Sodium hydroxide. Grams.	Rochelle salt. Grams.	Glyc- erol. cc.	Ammonia 0.90. cc.
Pavy.....	4.158	(7.20)	20.76	..	370
Hebner.....	4.502	15.6 19.5	22.49	..	370
Purdy.....	4.752	23.5 KOH(= 16.8 NaOH)	....	38	350
Peska.....	6.927	10.00	34.50	..	135

variations in the oxidizing power of each solution follow from alterations in the amount of fixed alkali or ammonia and this is shown in some tests to be now given. I made them as follows :

## A.

Copper sulphate, cryst.....	5 grams.
Caustic soda (100 per cent.) .....	18 "
Glycerol.....	35 cc.
Water, to make.....	250 "

## B.

Ammonia water .....	0.90 sp. gr.
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These solutions were mixed in the proportions given below and used in the titration of a 0.2 per cent. dextrose solution in the usual manner. The results are shown in the following table:

TABLE I.—REDUCTION WITH AMMONIA VARIABLE.

Vol. of Sol. A. cc.	Vol. of Sol. B. cc.	Vol. of water. cc.	Sugar solution required. cc.	Mg. of CuSO <sub>4</sub> .5H <sub>2</sub> O to 1 mg of C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> .	Mols. of CuO to 1 mol. C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> .
25	75	00	28.5	8.772	6.32
25	60	15	29.5	8.474	6.11
25	50	25	30.3	8.251	5.95
25	40	35	30.8	8.117	5.85
25	30	45	31.4	7.962	5.74

The oxidizing power varies greatly with the amount of ammonia present and is decreased with increase in the latter. The effect amounts to about 10 per cent. of the whole in the limits

of the effect of adding an excess of sodium or potassium hydroxide, even more marked as was found by experiments given above. The following solutions were made :

## C.

Copper sulphate, cryst .....	5 grams.
Glycerol .....	35 cc.
Water, to make .....	250 "

## D.

Strong ammonia water .....	0.90 sp. gr.
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## E.

Sodium hydroxide, 100 per cent .....	50 grams.
Water, to make.....	250 cc.

These solutions were mixed in different proportions and were used to test a dextrose solution of about 0.2 per cent. strength. The results obtained were as follows :

TABLE II.—REDUCTION WITH FIXED ALKALI VARIABLE.

Vol. of Sol. C. cc.	Vol. of Sol. D. cc.	Vol. of Sol. E. cc.	Vol. of water. cc.	NaOH in grams per liter Grams.	Sugar solution required. cc.	Mols. of CuO to 1 mol. C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> .
25	35	25	15	50	34.8	5.18
25	35	20	20	40	33.3	5.41
25	35	15	25	30	32.0	5.63
25	35	10	30	20	30.4	5.93
25	35	5	35	10	28.7	6.28
25	35	2.5	37.5	5	28.0	6.44

We have here an extreme variation of about 25 per cent. in the oxidizing value of the copper solution. As the fixed alkali itself possesses marked oxidizing power, as shown, in fact, in our ordinary Moore's test for sugar in urine, the increase in alkali must add to the oxidizing power of the finished solution. Fehner has shown that the solution can be made and will oxidize perfectly without the addition of any fixed alkali, but the action is then very slow and the oxidation ratio still lower.<sup>1</sup>

These experiments indicate that to secure anything like uniformity in the results obtained by the Pavy solution or its modifications, care must be taken to employ definite and constant amounts of fixed alkali and ammonia. The statement of Allen ("Chemistry of Urine," p. 67, 1895) that considerable variation in the amount of caustic alkali and ammonia may be made in the Pavy solution without altering appreciably its oxidizing value does not appear to be correct. Of the two cheap fixed alkali hydroxides, caustic soda is preferable to caustic potash and is much more commonly used.

Variations in the amount of glycerol or tartrate are of less importance, but still have an appreciable influence, as I have found in several trials. As the great excess of ammonia present is sufficient to hold the copper hydroxide in solution, it is not necessary to use a large amount of either.

In the Pavy and Purdy liquids the oxidizing power is apparently assumed to be independent of the strength of the sugar solution added. Pavy and Purdy assume the factor 8.316 grams of

<sup>1</sup> *Analyst*, 6, 219.

$\text{SO}_4 \cdot 5\text{H}_2\text{O}$  to 1 gram of  $\text{C}_6\text{H}_{12}\text{O}_6$ . But Peska has shown that factor varies over 2 per cent. with solutions ranging from 0.1 per cent. in strength.<sup>1</sup>

As in practical work it is desirable to employ a solution, 1 cc. which oxidizes some simple unit amount of sugar. I have used in the work below with a value of 1 cc. for each milligram sugar oxidized in 0.2 per cent. solutions. It is made with following amounts per liter:

Copper sulphate, cryst .....	8.166 grams.
Sodium hydroxide (100 per cent.) .....	15.000 "
Glycerol .....	25.000 cc.
Ammonia water (sp. gr. 0.9) .....	350.000 "
Water, to make .....	1,000.000 "

The value of this solution in copper oxide,  $\text{CuO}$ , is 2.6042 mms per liter, and 1 molecule of sugar = 5.88 molecules of  $\text{O}$ , as it is employed.

Of the solution, I use 50 cc. and dilute with water to 100 cc. to prevent too rapid an escape of ammonia and avoid reoxidation to some extent, I add to the mixture, while warming, enough pure white solid paraffin to make a layer of 3 or 4 mm. thickness when melted. The burette tip for discharging sugar solution or urine is made long enough to pass down neck of the flask and below this paraffin. By boiling gently and adding the weak saccharine liquid slowly, very close and constant results may be obtained. At the end of the titration paraffin is solidified by inclining the flask and immersing it in cold water, or by flowing cold water over it. The reduced liquid is then poured out and the cake of paraffin is thoroughly washed for the next test. A flask so prepared may be used for hundred titrations. The solid paraffin is much preferable to oil recommended by Allen and Peska. To prevent bumping and facilitate easy and uniform boiling, I add a few very small fragments of pumice-stone.

A solution made as above is not too strong in copper for accurate work, but the volume of ammonia necessary to hold a much larger amount of the reduced oxide in solution would render the process very inconvenient. The sugar employed in fixing the value of the above standard solutions was a very fine sample of

<sup>1</sup> *Ztschr anal. Chem.*, 35, 94.

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The crystal dextrose made for me by Dr. Gudemann, of the Chicago Sugar Refining Co. It was further purified by crystallizing in hot alcohol. After careful drying at 80° C., it was examined by a very accurate polarimeter and found to have a degree of purity not less than 99.9 per cent.

An ammoniacal solution made in this way and used with the aid of paraffin is preferable to the usual Fehling liquid in the detection of weak dextrose solutions. It cannot be conveniently used for strong solutions, however, because of the large volume of standard required to oxidize a small volume of the saccharine acid.

The behavior of this solution with the weak sugar solutions has now been established, it remains to show how it acts with creatinin and uric acid.

#### CREATININ AND COPPER SOLUTIONS.

The importance of creatinin as a reducing body is commonly overlooked although referred to in Neubauer and Vogel's "Urine Analysis," and in other large works. This is partly due to the fact that the amount present is generally underestimated, as shown by the figures given in several of our best own handbooks of urine analysis.<sup>1</sup> The reducing effect of creatinin on alkaline copper solutions has been observed by Hermann Müller,<sup>2</sup> Johnson,<sup>3</sup> and others. Müller places the reducing power low, 1 molecule of creatinin to not over 0.75 molecule of copper oxide.

Johnson states that 4 molecules of ordinary creatinin have the same reducing action on copper salts as 2 molecules of grape-sugar, and that this reduction plus that due to the uric acid will account for the whole of the reducing action found in normal urine. The presence of sugar is disputed. The results of Müller and Johnson, are widely divergent, which is doubtless due to essential differences in the methods of observation. The reducing power of creatinin is shown only after long warming in the ordinary Fehling titration, and at the outset the cuprous oxide formed is held in solution, which is a disturbing element making the test. But with the weak ammoniacal solution

<sup>1</sup> See on this point, Allen, *loc. cit.*

<sup>2</sup> *Ztschr. anal. Chem.*, 21, 610.

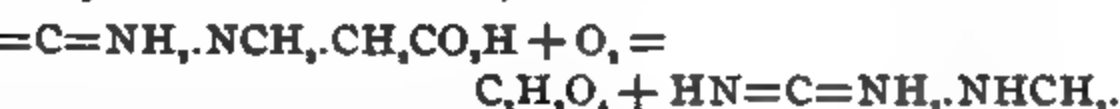
<sup>3</sup> *Chem. News*, 55, 304

for the sugar the behavior is quite different. The reduction appears to proceed as regularly and normally as with sugar. I have made a number of tests with solutions of different strengths, but all weak, and find that about 92 mg. of creatinin required for 50 cc. of the standard copper solution containing 2.604 grams of CuO to the liter. This corresponds almost exactly to the proportion, 1 molecule  $C_4H_7N_3O$  : 2 molecules CuO, which is about one-third the reducing power of dextrose under the same conditions. The result is much larger than that of Form Müller, but lower than the figures given by Johnson. The actual reducing values are given in the table below. The creatinin used was prepared in the laboratory and was practically

TABLE III.—REDUCING POWER OF CREATININ.

Creatinin 100 cc. Mg.	Copper solu- tion taken and diluted to 100 cc. cc.	CuO equiva- lent. Mg.	Creatinin solution used. cc.	Creatinin to 130.2 mg CuO. Mg.	Mols. CuO to 1 mol. $C_4H_7N_3O$ .
50	25	65.1	92.5	92.5	1.998
50	25	65.1	94.0	94.0	1.967
120	50	130.2	76.0	91.2	2.026
120	50	130.2	77.0	92.4	2.000
Mean,					1.998

The oxidation of creatinin by alkaline copper solutions is fully explained on the assumption that oxalic acid and methylhydrazine are formed, the creatinin being first converted into creatin by the alkaline solution,



In the above experiments, however, the amount of oxygen absorbed corresponds with only half that necessary for this equation, and under the condition none can come from the air. The reaction must therefore take place in a different manner, which appears all the more probable in view of recent work by E. Wörner<sup>1</sup> and Toppelius and Pommerehne,<sup>2</sup> who found that the reduction is variable with time of boiling with strong Fehling solution. In weak solutions the reduction is slow, but on boiling 5 cc. of weak creatinin solution an hour with 60 cc. of strong Feh-

<sup>1</sup> *Ztschr. physiol. Chem.*, 27, 1.

<sup>2</sup> *Archiv. der Pharmacie*, 234, 380.

ling solution a much greater effect is observed. Under such conditions 1 molecule of creatinin appears to reduce over 4 molecules of CuO. It is quite possible that the oxidation of creatinin is preceded in weak solution by hydrolysis with formation of ammonia and methyl hydantoin and that this body is afterwards oxidized in several stages. The reduction of 4 molecules of CuO would correspond to the oxidation of the acetic acid group in creatin to oxalic acid, as required by the equation written above, but in the ordinary application of the copper tests in urine analysis no such degree of oxidation is likely.

#### URIC ACID AND COPPER SOLUTIONS.

The behavior of uric acid with alkaline copper solutions has been described by several chemists and notably by Riegler<sup>1</sup> who studied the reaction with Fehling solution. He found, as a mean result of a number of experiments, that 1 gram of uric acid yields cuprous oxide corresponding to 0.800 gram of copper. On the assumption that 1 molecule of uric acid reduces 2 molecules of copper oxide the reduced copper obtained should amount to 0.7556 gram; the reduction therefore goes a little further than this theoretical relation.

The reducing action seems to be much more readily followed in the ammoniacal solution, however, and several tests were made to establish the relation under such conditions. The following are the details in tabular form:

TABLE IV.—REDUCING POWER OF URIC ACID.

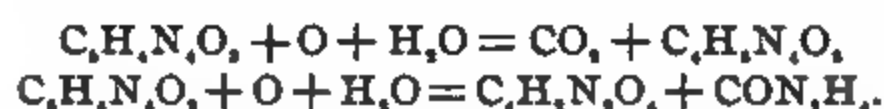
Uric acid in 100 cc. Mg.	Copper oxide taken.	Uric acid solution used. cc.	Uric acid to 130.2 mg CuO. Mg.	Mols. CuO to 1 mol. C <sub>5</sub> H <sub>4</sub> N <sub>4</sub> O <sub>3</sub>
80	39.8	36	94.2	2.92
80	65.1	58	92.8	2.96
120	130.2	76.5	91.8	2.99
120	65.1	37.8	90.8	3.03
				Mean, 2.98

The mean result of 1 molecule of uric acid to 2.98 molecules of copper oxide is essentially in the relation of 1:3, or 1 molecule of the acid to 1.5 atoms of oxygen absorbed. This is a larger amount of oxygen than corresponds to the reactions usually given for the oxidation of uric acid which is generally

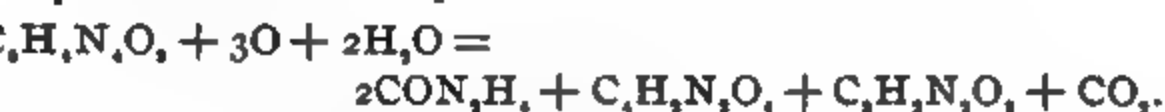
<sup>1</sup> *Ztschr. anal. Chem.*, 35, 31.



presented as taking place primarily in one of two directions, leading either to allantoin or to alloxan and urea. These reactions require each one atom of oxygen as follows :



Secondary reactions, however, doubtless take place resulting in the further oxidation of one or the other of these products and requiring more oxygen. Thus, from alloxan parabanic acid and other substances may be derived, and possibly are derived in the oxidation in question. A reaction leading to parabanic acid from the partial oxidation of the alloxan in the above case may be represented in this way :



Whether this reaction represents the course of the oxidation or not it remains true that the uric acid takes up more oxygen than is required by the simpler reactions given above. This is true also of a reaction in sulphuric acid solution referred to below. Having described the three important substances in urine which exert a reducing action on the ammoniacal copper solution, it remains to explain how the last two mentioned, along with urea and ammonia, the other important products of nitrogenous excretion, were practically determined in the investigation in hand. The amounts of these last substances are of interest in connection with the actual reducing compounds.

#### DETERMINATION OF CREATININ.

This body is most accurately obtained by precipitation from the prepared urine in the form of zinc chloride double salt. This is the method of Neubauer modified by Salkowski, but it is desirable to use as large a volume of urine as possible. In the work below I used, when available, 480 cc. which was treated with barium hydroxide to faint alkaline reaction and precipitated with barium nitrate in the cold. In a few cases milk of lime and calcium chloride were used in this preliminary treatment. The volume was then made up to 600 cc., filtered after half an hour, and of the filtrate 500 cc., representing 400 cc. of the original urine, was taken for the further work. Care was observed to

secure and maintain a nearly neutral reaction in this liquid so as to avoid, in the following evaporation, the conversion of creatinin into creatin. The final precipitate of the zinc chloride salt was collected on a Gooch crucible, dried at  $100^{\circ}$ , and weighed. From this weight that of the pure creatinin was calculated and this is given in the table below.

#### DETERMINATION OF URIC ACID.

Of all the methods now available, the Fokker-Hopkins process seems to give the most regular and trustworthy results. 100 cc. of urine are precipitated with about 30 grams of pure ammonium chloride, or enough to produce a saturated solution. The beaker containing the precipitate is allowed to stand in a cool place over night. Then the precipitate is collected on a filter and washed thoroughly with a saturated solution of ammonium sulphate to remove all chlorine. The filter is perforated and by aid of a jet of hot water the precipitate is washed into a flask. About 100 cc. of the water should be used. To this turbid liquid 20 cc. of pure strong sulphuric acid is added, and then, without delay, twentieth-normal permanganate solution from a burette until a faint pink tinge is secured which is permanent several seconds. For this stage of the reaction Hopkins gives 1 cc. of the twentieth-normal permanganate as corresponding to 3.75 mg. of uric acid. By waiting and adding more permanganate from time to time, as the color fades, a considerably larger volume may be used, for which no factor has been worked out. For the direct oxidation, using 1 atom of oxygen to 1 molecule of uric acid, each cubic centimeter of the twentieth-normal permanganate solution should correspond to 4.2 mg. of the acid instead of 3.75 mg. The results obtained by taking a later reading correspond more nearly to an oxidation with 1.5 atoms of oxygen to each molecule of acid, but they are not definite enough for calculation. The Hopkins factor has therefore been used, and, it is believed, with a considerable degree of accuracy, since numerous blank experiments were carried out with pure uric acid to fix the point for observation of the end color.

#### DETERMINATION OF UREA.

This has been carried out by the two common methods, the Liebig process by titration with mercuric nitrate, giving properly

ough measure of the total nitrogen rather than the urea itself, and by the Knop-Hüfner hypobromite or hypochlorite process. The results of the first method are always too high if calculated as urea, while those of the latter are too low. As the last process was carried out it was assumed that 95 per cent. of the urea present was decomposed normally according to the equation



calculations being made accordingly from the experimental results. The observations were made in a Lunge nitrometer, gas volumes obtained being always reduced to standard conditions. Even with the various corrections the results were considerably lower than those by the Liebig process because of the inherent positive errors in the latter. Something will be said about this below when the experimental results are discussed.

#### DETERMINATION OF AMMONIA.

Of all the processes recommended for the determination of the small amounts of ammonia found in urine the most reliable is the old Schloesing method of liberation by milk of lime and absorption by standard acid, under a bell-jar. The urine, about 10 cc., is measured into a glass crystallizing dish and mixed with an excess of milk of lime. Over this dish a glass evaporating dish containing a small known volume of standard sulphuric acid is supported on a triangle. The whole is covered without delay with a clean glass bell-jar, resting on a glass plate and is allowed to stand three days for the liberation of the ammonia, and its absorption by the titrated acid. At the end of the time the bell-jar is washed out with a little water which is added then to the dish with the standard acid. This is finally titrated and the loss in acidity measures the ammonia absorbed; while the process is very slow little or no risk is incurred of decomposing urea or other substance containing nitrogen and thus liberating an excess of ammonia. It is, of course, necessary to operate on fresh urine, as the object is to measure that normally present, and not that which may be made by the alkaline fermentation of urea. The results are always a little low, because a small portion of the ammonia escapes either liberation or absorption. To determine the probable error here a number of experiments were made with weak ammonium chloride solutions, corresponding in ammoniacal

strength to normal urine. These experiments gave very concordant results from which it appeared that after three days' time, at the temperature of the tests, 90 per cent. of the ammonia present was liberated and absorbed by the acid. In all the experiments below the results obtained were corrected by the aid of this factor.

Table V, following, gives the result of examinations of a number of normal urines, embracing determinations of the above-described constituents. These urines were collected so as to secure the whole day's excretion and were kept cold until the full twenty-four hour sample was obtained. The analysis was then begun immediately, and finished as speedily as possible. Fifty cc. of the standard copper solution were always employed in the reduction test, and the following table gives the volume of urine required to reduce this under the conditions described above. The reaction of the mixed day's urine was always acid and all samples, except No. 7, were of the usual normal yellow color. This sample was dark, probably because of its concentrated condition. It will be noted that the average total volume is smaller than is usually assumed as the mean daily excretion.

TABLE V.—RESULTS OF URINE ANALYSES.

No. of sample.	Excretion in twenty-four hours.	Specific gravity at 20°.	Urine required to reduce 50 cc. of copper solution.	Ammonia from 1000 cc. of urine.	Uric acid from 1000 cc. of urine.	Creatinin from 1000 cc. of urine.	Urea from 1000 cc. of urine by the Liebig process.	Urea from 1000 cc. of urine by the Knop-Hüfner process.
1	1230	1.031	21.0	645.0	840.0	1930	30.50	....
2	1450	1.035	21.2	522.0	743.0	1876	25.60	....
3	845	1.027	23.6	654.8	832.5	1268	38.80	....
4	1920	1.019	22.5	427.0	646.0	851	25.75	....
5	1950	1.023	20.2	465.0	678.0	1681	24.74	23.72
6	1200	1.025	20.5	593.1	619.0	1195	29.69	27.66
7	765	1.024	18.9	526.6	637.5	961	31.10	27.46
8	1775	1.020	58.0	227.7	....	653	12.90	....
9	1020	1.030	14.9	858.8	971.2	1750	39.18	37.27
10	1280	1.018	27.3	408.0	423.7	1016	17.57	14.83
11	1090	1.024	23.3	631.0	510.0	1374	25.04	24.54
12	1190	1.025	25.6	431.7	611.0	1381	32.72	29.72
13	915	1.025	21.1	711.7	630.0	1604	28.17	25.56

Excretion in twenty-four hours.	Specific gravity at 20°.	Urine required to reduce 50 cc. of copper solution.	Ammonia from 1000 cc. of urine.	Uric acid from 1000 cc. of urine.	Creatinin from 1000 cc. of urine.	Urea from 1000 cc. of urine by the Liebig process.	Urea from 1000 cc. of urine by the Knop-Hufner process.
		cc.	Mg.	Mg.	Mg.	Grams.	Grams.
1440	1.015	27.8	522.0	491.0	868	17.67	15.85
1220	1.029	21.2	716.0	671.0	757	26.46	20.94
1200	1.025	19.7	711.6	712.5	1735	32.11	31.23
800	1.030	17.9	669.0	693.8	1681	34.23	30.29
900	1.022	23.7	488.7	581.3	1239	21.91	17.83
1100	1.027	18.1	507.7	581.2	1898	26.32	21.73
835	1.032	17.1	1001.0	1020.0	1417	39.10	34.68
900	1.023	17.4	569.4	626.0	2224	26.63	23.66
970	1.026	23.4	374.8	521.0	976	18.61	16.15
1600	1.018	28.0	601.6	416.2	926	19.30	17.60
1120	1.027	20.7	811.3	701.2	1477	24.55	22.47
1167	1.025	23.0	602.0 <sup>1</sup>	658.7	1392 <sup>1</sup>	27.68 <sup>1</sup>	24.37

The analytical results as obtained are given in Table V. As might be expected, are quite variable, and at first do not reveal any relationship that appears characteristic. For a better comparison I have stated the amounts of urea, uric acid, ammonia, and creatinin found in grams or milligrams per cc. rather than for the excretion of twenty-four hours. In Table VI, I have calculated the total reducing power in terms of cc. of 10% solution for 1000 cc. of each urine, and have then done the same for uric acid and creatinin, basing the calculation on the assumption that under the conditions of the experiments each molecule of uric acid reduces 3 molecules of copper oxide and each molecule of creatinin reduces 2 molecules of the oxide. The sum of these two reductions is given in a separate column, and finally the ratio of this to the total reduction is given in the last column.

No. 8 not included.

TABLE VI.—RELATION OF REDUCING POWERS.

No. of sample.	Total reducing power of 1000 cc. of urine in grams of CuO.	Reducing power of the uric acid in 1000 cc. of urine in grams of CuO.	Reducing power of the creatinin in 1000 cc. of urine in grams of CuO.	Sum of the uric acid and creatinin reductions.	Relation of the uric acid and creatinin reductions to total reduction.
1	6.200	1.194	2.719	3.913	0.631
2	6.141	1.056	2.643	3.699	0.602
3	5.517	1.184	1.786	2.970	0.538
4	5.787	0.911	1.199	2.110	0.365
5	6.446	0.964	2.368	3.332	0.517
6	6.351	0.880	1.684	2.564	0.404
7	6.889	0.906	1.354	2.260	0.328
8	2.245	....	0.920	....	....
9	8.738	1.381	2.370	3.751	0.429
10	4.769	0.602	1.432	2.034	0.427
11	5.588	0.725	1.936	2.661	0.476
12	5.086	0.869	1.946	2.815	0.554
13	6.171	0.896	2.260	3.156	0.511
14	4.684	0.698	1.223	1.921	0.410
15	6.141	0.954	1.066	2.020	0.329
16	6.609	1.013	2.444	3.457	0.523
17	7.291	0.986	2.369	3.355	0.460
18	5.494	0.826	1.746	2.572	0.468
19	7.192	0.825	2.674	3.499	0.487
20	7.614	1.417	1.997	3.414	0.448
21	7.483	0.890	3.133	4.023	0.538
22	5.564	0.741	1.375	2.116	0.380
23	4.650	0.592	1.305	1.897	0.408
24	6.290	0.997	2.081	3.078	0.489
Means,	6.204	0.935 <sup>1</sup>	1.961 <sup>1</sup>	2.896	0.466

From the mean values given at the foot of the last table several interesting relations may be established. As in the ammoniacal solution 1 molecule of dextrose reduces 5.88 molecules of copper oxide, the above average reduction corresponds to 2.836 grams of sugar per liter, or about 0.28 per cent. The uric acid amounts to 0.658 gram per liter, or 0.065 per cent. The creatinin is equivalent to 1.392 grams per liter or 0.136 per cent. The data of the last column show that a large portion of the total reduction is due to the action of these latter products.

<sup>1</sup> No. 8 not in averages.

in the mean, amounts to 46.6 per cent., which calculated sugar is equivalent to 1.322 grams per liter, leaving 1.514 as the amount of sugar possibly present. This, however, presents a maximum value, as there are unquestionably traces of other bodies present which, like the uric acid and creatinin, have a reducing action. If the effect of these could be estimated it is likely that the reducing power, in the mean, would be found to be pretty evenly distributed between the saccharine and non-saccharine products.

It is not possible to draw any very exact general conclusions from the figures of the above table connecting the numerical results with the character of the food of the individual or with any other factor. Most of the urines were obtained from young students or teachers, and all pretty well nourished. It may be noticed, however, that the urines showing the highest reduction ratio for uric acid, and creatinin, as compared with the sugar reduction, were from men with the strongest physique with diets containing much meat. On the other hand the lowest reduction ratios for uric acid, and creatinin correspond to cases of slighter physique and lower nutrition. Urines Nos. 1 and 2 were from men consuming a diet largely of meat. No. 15 was from the same individual some weeks later after a change of diet to bread and vegetables largely. But from most of the urines no characteristic relation is apparent; another series of investigations is in progress in which the question of food in relation to the reducing power is being more closely determined.

#### RATIO OF UREA TO URIC ACID.

This ratio is more important and more characteristic than is the absolute amount of the acid. In the older works on urine analysis or physiological chemistry it was always stated too high, usually as 50:1 or 60:1. This is due to the fact that the amount of uric acid was generally underestimated, while that of urea was naturally overestimated if found by the Liebig process, and not corrected.

In making an examination of a fraction of the day's excretion, instead of on the mixed twenty-four hour sample, a false ratio is usually found because the urea and uric acid are not eliminated at a constant rate following ingestion of food. The ratio

from the above table is 36.9:1 if we consider the urea as measured by the Knop-Hüfner process and 42:1 if we take the uncorrected values for urea as found by the Liebig process. The results here are in the mean about 10 per cent. high as may be shown when we take into consideration the effect of the other nitrogenous bodies, especially the ammonia, uric acid, and creatinin, on the mercuric nitrate solution. With such a correction subtracted the amount of urea approaches closely that found by the gas volume method and the ratio becomes again about 37:1; this result is in accord with the average normal ratio as found in experiments on the excretion of the twenty-four hours as made by Hopkins and others. See an interesting paper by Hopkins and Pope<sup>1</sup> in which variations in the excretion of urea and uric acid in relation to kind of food and time of meals is discussed.

#### THE AMOUNT OF AMMONIA.

The ammonia in 1000 cc. of urine, as shown by the above figures, is, in the mean, 602 mg., but the individual variations are between 228 and 1001 mg. These correspond roughly to the variations in the other nitrogen bodies. The average daily excretion is seen to be 703 mg. The daily extremes are 364 and 908 mg. The average correction to be applied to the Liebig urea titration on account of the ammonia present is about 1.2 cc. of the usual standard mercuric nitrate solution. This result was found in experiments carried out on the titration of urea solutions containing small amounts of added ammonia, and is somewhat lower than the factor given by Feder.<sup>2</sup> Experiments are now in progress to determine more definitely the behavior of uric acid and creatinin in this titration, the statement in Neubauer and Vogel's Harnanalyse<sup>3</sup> requiring, apparently, a slight correction.

#### THE DAILY AVERAGES.

The numbers above given are expressed, for convenience in comparison, in grams or milligrams per liter. The values for the daily excretion are often interesting and these will now be given as calculated from the volumes collected in the twenty-

<sup>1</sup> *Journal of Physiology*, 23, 271.

<sup>2</sup> Neubauer and Vogel's Harnanalyse, 9th German edition, p. 519.

<sup>3</sup> *Loc. cit.*



ur hours as shown by the figures of the second column in table V.

TABLE VII.—MEAN RESULTS FOR DAILY EXCRETION.

Volume excreted .....	1167.00	cc.
Total reduction, equivalent to.....	3.31	grams $C_6H_{12}O_6$ .
Uric acid and creatinin reduction equivalent to .....	1.54	" "
Remaining reduction equivalent to.....	1.77	" "
Amount of ammonia.....	0.703	gram.
Amount of urea (mean of gas method and Liebig, corr.) .....	29.75	grams.
Amount of creatinin.....	1.624	"
Amount of uric acid.....	0.799	gram.

The urines examined in the above experiments were all normal and represent the excretion from average meat and vegetable diet. In a following paper I will give results obtained from urines of consistent vegetarians, noting the same relations. Most of the experimental work detailed above was done by Mr. Frank Wright, assistant in the laboratory of physiological chemistry, and Mr. Charles Ericson, to whom my thanks are due.

NORTHWESTERN UNIVERSITY,  
CHICAGO, April 24, 1900.

## AN EXAMINATION OF BROWN AND TAYLOR'S OFFICIAL METHOD OF IDENTIFYING BUTTER.

BY JOHN A. HUMMEL.

Received March 7, 1900.

THE recent great increase in the production of renovated butter, due probably to the improvements in the method of manufacture and the prevailing high price of creamery butter, has necessitated, in several states, the enactment of laws regulating its sale. Since the enactment of these laws there has been some discussion as to reliable methods for its identification. The fact that the chemical properties and the proximate composition of samples examined are entirely within the range of normal butter, has directed attention to its physical properties more particularly its behavior with polarized light. As is already well-known, in the manufacture of renovated butter, the butter-fat is melted and then cooled rather rapidly in a stream of cold water. This melting and rapid cooling induces a semicrystallization of

the fat. It was thought that this fact might be taken advantage of and would at least deserve some study. For the experiments carried on in this laboratory fifteen samples of renovated butter secured from factories in St. Paul, Minneapolis and Duluth were used; as many samples of undoubted normal butter from Minnesota creameries and dairies were also examined. The preparations for the microscopic examination were made by simply placing a small bit of the butter on a glass slide and pressing it into a thin film with a cover-glass. The preparation was then immediately examined with a polarizing microscope giving a magnification of 120 to 150 diameters. A selenite plate was placed between the slide and the lower nicol. In every case the normal butters gave with the selenite which was used a uniformly blue colored field, showing the entire absence of fat crystals. The renovated butters on the other hand gave a blue field mottled with yellow; this mottled appearance varied slightly in intensity but was very marked and distinctive in every case. The accompanying photomicrographs are from representative preparations and are believed to be fair averages. In making these photomicrographs the selenite was not used, the thin film of butter being simply placed between crossed nicols. The source of light was a 16 candle-power incandescent electric light, and an exposure of fifteen minutes was necessary for the normal butter, eleven minutes for the renovated butter, and eight minutes for the oleomargarine, using plates of medium rapidity.

The writer is well aware of the severe criticism directed against the method proposed by Dr. J. Campbell Brown, and later by Dr. Taylor, for identifying adulterated butter by means of the microscope and polarized light, yet he has found a microscopic examination of great value, and believes it to be one of the best methods for the identification of renovated butter, as found upon the Minnesota markets at least. In the course of work in this laboratory 247 samples of butter have been subjected to a microscopic examination as outlined above and out of this number 58 showed conclusive evidence of having been melted and cooled as in the process of renovating. A majority of those samples which could be traced to the manufacturers were admitted as being renovated and some fines have been imposed.

**Fig 1. Normal Butter**

**Fig 2 Renovated Butter**



**Fig 3. —Oleomargarine**



In the examination of these samples the greatest reliance was placed in every case on the microscopic appearance, though other tests were also used.

LABORATORY OF THE MINNESOTA STATE DAIRY AND FOOD COMMISSION.

[FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, PATHOLOGICAL  
INSTITUTE OF THE N. Y. STATE HOSPITALS.]

### ON THE PREPARATION OF NUCLEIC ACIDS.<sup>1</sup>

BY P. A. LEVENE.

Received April 14, 1900.

THE various modifications of Altman's and Kossel's methods of obtaining nucleic acid, which have appeared during the last year clearly demonstrate two facts: first, that the old methods were unsatisfactory; and secondly, that a thorough knowledge of the nucleo compounds is of ever-increasing importance to all investigators in the field of the chemistry of the cell.

All the new methods published in recent years are based on two properties of the nucleic acids; namely, their solubility in acetates and their resistance to dilute alkalies on heating. Both properties were observed only by the authors of the new methods. The improvement recently advocated by Schmiedeberg was based on the idea of removing (by means of copper salts) the proteid material which combines with the nucleic acids, to form the nucleo-compounds occurring in cells and tissues.

One of the properties of the nucleic acids described by the more recent investigators, namely their resistance to heating with alkalies, stands in contradiction to the observations of the older workers. Thus Miescher considered it requisite that the material which was being treated for nuclein should be kept at a very low temperature during every phase of its preparation. Kossel has succeeded in decomposing the ordinary nucleic acid of the thymus into thymic acid by heating it in water on the water-bath.

Neuman, advocating the heating method with alkalies, states that by this method more than one acid is generally obtained. From the fact that different proportions of the acids vary with the duration of heating, he draws the conclusion that the three acids are modifications of the one occurring in the tissue.

<sup>1</sup> Read before the New York Section of the American Chemical Society, April 6, 1900.

Hammarsten and Bang, who have applied the method of heating with alkalies for obtaining their guanilic acid, obtained a substance with properties differing greatly from those of all the other acids hitherto described.

Thus from the statements of the investigators advocating the "hot" method it may be admitted that the new methods, being an improvement over the old ones, they may be still further perfected, because they do change somewhat the original character of the substance.

In addition to this, I would like to add that to some nucleo-compounds the new method cannot be applied at all, as their decomposition on heating with very dilute alkalies takes place in so short a time that it is impossible to obtain any satisfactory yield by that method. I refer to the compounds known as para-nucleo-compounds.

A uniform method for obtaining all the nucleic acids is, however, most desirable. During the last two years I have been engaged in the study of different nucleo-compounds, and I have used, with satisfactory results, a method differing from those used by other authors. Fresh tissues, nucleo-proteid, as well as para-nucleo-proteids are treated with a strong solution of alkalies (5 per cent. sodium hydroxide or 8 per cent. ammonia), and allowed to stand in a cool place one to two hours. This solution or mixture is then gradually and slowly neutralized with acetic acid, care being taken not to add too much acid at a time, so that the temperature of the solution does not rise too high. It is advisable to keep the solution in a cooling mixture or to add ice to the alkaline mixture itself. When the mixture remains only slightly alkaline a saturated solution of picric acid is added until the mixture becomes neutral or nearly neutral (about 75 cc. of the picric acid to 1 liter of the mixture is generally sufficient); more acetic acid is added until the mixture is rendered strongly acid and then allowed to stand for some time, filtered, and to the filtrate is added 95 per cent. alcohol until the latter ceases to form a precipitate. This precipitate is nucleic acid. The picric acid is added in order to remove the proteid material. On neutralization with acetic acid a sufficient quantity of acetates is formed to enable the precipitation of all the nucleic acid by means of alcohol. (In the absence of acetates nucleic acid cannot be pre-



precipitated by alcohol.) By this method I have treated ovovitellin, ichtulin of cod-fish eggs, cod-fish sperm, pancreas and bacillus tuberculosis.

The very crude acid obtained from the ovovitellin contained 9.65 per cent. of phosphorus; three other samples purified contained, 10.02, 9.95, and 9.79; a copper salt contained, P, 8.57, and Cu, 12.36 per cent.; for the free acid, P = 9.78 per cent. The acid obtained from the same vitellin by Milroy in Kossel's laboratory varied in its contents of phosphorus from 7.51 to 7.94 per cent. The acid obtained from ichtulin contained 8.46 per cent. of phosphorus. Walter, who studied the chemical nature of ichtulin in Kossel's laboratory, failed to obtain from it a substance similar to nucleic acid. The acid obtained from the cod-fish sperm was biuret free after the first precipitation and contained 8.65 per cent. of phosphorus. From the pancreas an acid was obtained with the same solubility as the other nucleic acids, while the substance described by Bang as guanilic acid differed in that respect from the other nucleic acids. From the bacillus tuberculosis the acid was also obtained biuret free after the first precipitation.

The study of the chemical properties of all the above-mentioned acids is now in progress.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 25.]

### A CHROMIUM CELL FOR THE RECTIFICATION OF ALTERNATING CURRENTS.

BY J. LIVINGSTON R. MORGAN AND W. A. DUFF.

Received April 17, 1900.

MUCH attention has been given of late to aluminum rectifying cells. These consist of a platinum and an aluminum electrode in a solution of sulphuric acid or potash alum. When

the current is applied to such a cell, the aluminum electrode being the anode, the aluminum plate becomes covered with a highly resistant film which prevents, to a great extent, the further passage of the current in this direction. In the opposite direction however, *i. e.*, from platinum to aluminum through the liquid, the resistance of the electrolyte alone is encountered. If an alternating current is applied to such a cell, keeping the voltage down below a certain minimum point, an interrupted current, made up of the half waves of the alternating one, is the result. If the alternating voltage is increased gradually a point is finally reached at which the resistance of the film is overcome and the latter broken down after which the alternating current goes through unchanged. Up to this breaking-down point the current becomes less and less asymmetrical; *i. e.*, the opposite half waves become more and more alike in size. The minimum electromotive force which will cause the film to break down has been found by us as well as by others to be about 26 volts.

Our experimental work on this subject was done in the early part of 1899, but as it was not published at the time most of our results have since been found and published by others. The substitution of chromium for aluminum, however, has not yet been reported so that we propose to give our results very briefly here. At the time we did not expect to find any connection with the work of Hittorf<sup>1</sup> on chromium, but since such a one has been found we deem the result worthy of a short description for its bearing upon the general behavior of metallic chromium. Since our work was suspended in April, 1899, the results are fragmentary but we think of their kind, conclusive.

The electrolyte used throughout was 10 per cent. sulphuric acid. The chromium electrode consisted of a fragment of the chemically pure metal<sup>2</sup> fused into a glass tube containing mercury by which the connection was made. The platinum electrode was made of a strip of foil. The apparatus consists simply of a graded source of direct current, the amount going through the cell being measured by a low reading ammeter (0—5). A reversing switch is also used by which either the chromium or platinum may be made the anode. If the platinum

<sup>1</sup> *Ztschr. phys. Chem.*, 25, 729, and 30, p. 481.

<sup>2</sup> Rimer and Amend.

is first made the anode, the solution becomes yellow, and hydrogen gas is given off at the chromium electrode. If the chromium is now made the anode we find that no current goes through the cell, while when the platinum is the anode the current passes freely. We have then an asymmetrical resistance. *Using the chromium as anode and increasing very gradually the impressed electromotive force it is possible to stop any current entirely, as far as readings on the ammeter are concerned, until the pressure of about 75 volts is reached.* It is not difficult to stop this amount after the cell has once stopped it, but in starting, if the increase is made too rapidly, the current will force its way through. Of course, with the platinum as anode the resistance offered is only that of the sulphuric acid, so that the current is rectified with great efficiency.

When the increase in the electromotive force is made so rapidly that the current goes through from chromium to platinum, or after the cell breaks down by the application of more than 75 volts, a very peculiar result is obtained, and it is by this that Hittorf's results for the "active" and "inactive" states of chromium are confirmed. *Unlike the aluminum cell after it has broken down the chromium cell is still an asymmetrical resistance, but only when the platinum plate is made the anode. With chromium as the anode the current now passes freely.*

*If in this condition the cell is broken down by the application of too high an electromotive force to the platinum anode another reversal takes place so that about 75 volts can again be stopped using the chromium as anode.* The electromotive force necessary to cause this second reversal does not seem to be fixed, but the reversal always takes place. This change in the behavior of chromium is doubtless due just as were Hittorf's to the change from the "active" to the "inactive" state, and the change can be well shown experimentally in this way.

One other thing, we think, is proved by this work. Since chromium and aluminum act very much alike chemically, we should expect that they would both act asymmetrically in a cell and for the same reason. Aluminum has been supposed to act by a resistant layer of an oxid<sup>1</sup> and since chromium, when used in the same way, causes a reversal of the asymmetrical effect and

<sup>1</sup> Norden: *Ztschr. Elektrochem.*, 6, 159 and 188.

according to Hittorf its "active" and "inactive" states are not caused by resistant films, hence the asymmetrical effect of aluminum can only be caused by these; so that the theory of the action of the aluminum cell, as due to the formation of a resistant film, is confirmed.

## REMARKS ON SOME METHODS OF DETERMINING CARBON IN STEEL.<sup>1</sup>

BY GEORGE AUCHY.

Received April 25, 1900.

IN Blair's "Chemical Analysis of Iron"<sup>2</sup> it is stated that combined carbon in steel can be determined by loss upon ignition, 70 per cent. of the loss representing the carbon. As Blair gives the percentage of carbon in the carbon sponge as "about" 70 per cent., and as the method is not in general use, it may be inferred that it is known to be inexact. Mr. George Dougherty, in the *Iron Age* for May 11, 1899, proposes a method which is identical except that the carbon sponge is washed four times with hot nitric acid (sp. gr. 1.13) to dissolve out copper and copper sulphide. It may be questioned whether this procedure makes the method an accurate one as Mr. Dougherty's article does not throw much light on this point (only one result being given). Some experiments were made by the writer, which showed that, on the contrary, the washing with hot nitric acid is itself a source of error in one particular, and a possible source of error in another. 1. The hot nitric acid dissolves some of the carbon, and the amount dissolved varies with different steels. 2. The carbon sponge absorbs and retains a portion of the nitric acid, and this absorption is possibly not uniform in all cases. That the washing with hot nitric acid (sp. gr. 1.13) four times dissolves out carbon, and in varying amount, is shown in the following results, all from different steels:

<sup>1</sup> Read at the February Meeting of the Philadelphia Section.

<sup>2</sup> Blair's "Analysis of Iron," second edition, p. 151.

By combustion as usual. Per cent.	By combustion but washed with hot nitric acid. Per cent.	Percentage of loss	Carbon sponge boiled up or digested with hot nitric acid.
1.078	1.03	4.45	....
0.76	0.76	0.00	...
0.715	0.68	4.90	....
0.72	0.697	3.20	....
0.81	0.775	4.32	0.628 (Boiled up.)
0.665	....	....	0.62 (Digested one-fourth hr.)
0.665	....	....	0.56 ( " two hours.)

Eleven other similar results were obtained in which the lowest percentage of loss was 2.15, and highest 5.74. On digesting a carbon sponge with hot nitric acid (sp. gr. 1.13), and filtering the filtrate after boiling to expel lower oxides of nitrogen, decolorized permanganate solution.

That the carbon sponge, when washed with hot nitric acid (sp. gr. 1.13), absorbs and retains nitric acid, is indicated by the following results:

No.	Weight of carbon sponge. usual. Gram.	Weight of carbon sponge. Washed as usual. Gram.
723	0.0856	0.0955
691	{ 0.0583 0.0583	0.0647
723	0.0856	0.0880
739	0.0654	0.0747
740	0.0674	0.0742
BG2	0.0603	0.0750
737	0.0679	0.0740

No effort was made to ascertain whether the absorption was uniform in all cases. Instead the following determinations were made with a view to ascertaining the average percentage of carbon in the carbon sponge<sup>1</sup> and also at the same time the range of error in the process.

<sup>1</sup> Mr. Dougherty gives the percentage as 0.6750. This does not represent the absolute percentage of carbon in the nitric acid-washed carbon sponge, but the absolute percentage, plus the loss of weight, in terms of carbon, suffered by the paper disk in being washed by acid liquids, plus the loss in weight through the solubility of the carbon in the hot nitric acid wash. Nor does the writer's average factor (0.6000) represent the absolute percentage of carbon in the carbon sponge, but the percentage plus the loss by washing with hot nitric acid. The writer's filtrations were made through asbestos.

No.	1012	1013	1014	1015	1016	1017	Standard
Factor	{ 0.6319 0.6333	{ 0.6415 0.5845	{ 0.5950 0.5898	{ 0.5698 0.5897	0.5976	0.5575	0.6044 Average 0.6000

From the above it is seen that in a 0.60 per cent. carbon steel, results by this method might vary from 0.557 per cent. to 0.641 per cent. carbon, taking 0.6000 to be the factor. In the above tests only two washings with hot nitric acid (sp. gr. 1.13) in each case were made, in the lower row of tests, and three in the upper row to reduce the error from this cause as much as possible. The steels used were Swedish band saws containing not over 0.008 per cent. sulphur. If Meineke is right in considering the sulphur of the steel to be present in the carbon sponge in the free condition,<sup>1</sup> another source of error must be counted against the process when used for high sulphur steels.

#### THE USUAL COMBUSTION METHOD.

Professor D. H. Browne,<sup>2</sup> in describing the apparatus for the moist combustion method, says: "It is very necessary to have a small U-tube containing CaCl<sub>2</sub> in one leg and soda-lime in the other attached to the potash bulbs and weighed with them. The small straight tube designed to contain CaCl<sub>2</sub> attached to the potash bulb is not sufficient to prevent the escape of a slight quantity of water from the potash solution." Mr. A. A. Blair, in using the dry method, found that the calcium chloride tube did not absorb all the moisture drawn over from the potash bulb.<sup>3</sup> Mr. J. M. Camp, of Carnegie Steel Co., considers it necessary to have a weighed potash bulb containing strong sulphuric acid attached to the calcium chloride prolong.<sup>4</sup> The writer of this article several years ago described to this Society some experiences of this kind in using the wet method of combustion. The carbon dioxide was not completely absorbed by the potash solution (sp. gr. 1.27), and the moisture not completely retained by the prolong and drying train; the amount of moisture not retained by the drying train and passing into the potash bulb amounting to about 0.065 per cent. in terms of carbon with two sets of bulbs and prolongs in use, was 0.045 per cent. for the first set usually, and 0.02 per cent. for the second, and a correction to this amount

<sup>1</sup> *Ztschr. angew. Chem.* (1888), 376.

<sup>2</sup> *J. Anal. Appl. Chem.*, 8, 338.

<sup>3</sup> *Ibid.*, 8, 128.

<sup>4</sup> "Methods of Iron Analysis."

had to be made in each result. Professor Arnold also in his experience found a correction of 0.045 per cent. (using one bulb) to be necessary.<sup>1</sup> Professor Chas. F. Mabery found a loss of moisture and suspected a loss of carbon dioxide.<sup>2</sup> This seems to be sufficient evidence that the usual drying and absorbing agencies are inefficient. On the other hand, many chemists using both methods of combustion, have, like Dr. Drown, satisfied themselves by actual trial of the efficiency of their apparatus in this respect. The writer himself upon changing to the dry method found no further difficulty of this kind of any great consequence<sup>3</sup> except at first due to the copper oxide being packed into the pre-heating furnace too tightly, and aspiration being made by the pump. Mr. Buck, of the Bethlehem Steel Co., and Mr. Sargent, of the Carpenter Steel Works (the former with a Shimer apparatus, the latter with a modified oxygen apparatus), use extremely rapid rates of aspiration (allowing only twenty minutes for a combustion) without loss, either, of carbon dioxide or of moisture. Yet it is certain that those of us who have experienced a lack of efficiency of this sort have not simply dreamed or imagined it. What, then, is the reason that the potash solution sometimes fails to absorb all the carbon dioxide, and the calcium chloride or strong sulphuric acid fails to absorb all the moisture? Some recent experiments by the writer suggest an explanation and indicate a source of error, which though very simple may easily be overlooked. This source of error apparently lies in the fact that when there is undue resistance to the passage of gas through the apparatus for any reason, usually because of the calcium chloride or copper oxide having become clogged up in use, or having been packed in too tightly, or too finely divided in the first place, the gas then bubbles through the potash solution and the strong sulphuric acid, and passes through the calcium chloride not evenly and regularly but the reverse, and although precisely the same volume of gas may pass through as in normal conditions, the contact of gas with drying and absorbing materials is obviously less than normal.

<sup>1</sup> "Steel Works Analysis." Professor Arnold thinks this due to something generated in the combustion flask, but the writer obtained the same result by simply aspirating air through the apparatus for the same length of time.

<sup>2</sup> This Journal, 20, 510.

<sup>3</sup> Some moisture escaped from the prolong after being in use a number of tests, but this is now believed to be due to a cause that will appear later on.

This irregularity of action and accompanying loss may be due simply or mainly to the size and shape of the potash bulb, or may have its origin in the oxygen cylinder; but whatever the cause it seems to be a fact that when the gas does not pass freely and easily through the apparatus, and does not bubble evenly and regularly through the bulbs, loss ensues if a rapid or moderately rapid flow be allowed.

The experiments were as follows:

No	Prolong clogged up.	Prolong in good condition.
	Carbon. Per cent.	Carbon. Per cent.
1012	0.715	0.76
1013	0.68	0.716
1015	0.705	0.718

In the last experiment with clogged prolong the rate of speed of gas flow was diminished. With fresh calcium chloride in the prolong the following tests were made. The loss was believed to be due to the resistance offered to the passage of the gas by the 3 inches of rather closely packed copper oxide in the combustion tube.

Steel "S," usual rate.	Steel "S," slower rate.
Carbon. Per cent.	Carbon. Per cent.
1.053, 1.066, 1.06	1.078, 1.076, 1.077
1.067, 1.07, 1.065	.... ....

The first result under "usual rate" is not the writer's, but that of another chemist, and may perhaps be taken as an indication of some impediment to the flow of gas in his apparatus also. These results and the preceding ones seem to show that it is highly important to have the gas pass through the apparatus freely and easily if it is desired to maintain a rapid or moderately rapid rate of gas flow. Using another apparatus (a Shimer apparatus) in which the flow of gas is very free and unobstructed, no higher results could be obtained by using a slow rate than by using a rapid rate of gas flow. With the first-mentioned apparatus the writer now uses a rate of one bubble per second through the first or purifying bulb for one-half hour followed by ten minutes of a faster rate, and believes this rate slow enough not only to counteract the density of the copper oxide but also to allow for any clogging up of the calcium chloride that may occur; but this slow rate is, of course, impracticable where many combustions have to be crowded into



a day, or when a combustion must be made in the very shortest possible time; when a rapid rate is employed it would seem imperative to be sure that the gas passes freely and easily through the apparatus, and bubbles regularly and evenly through the potash bulbs. Calcium chloride sometimes clogs up and strong sulphuric acid seems preferable. The writer believes that for the calcium chloride prolong, one could profitably substitute diminutive bulbs for strong sulphuric acid of the Geissler type but constructed to hang instead of to stand so as to allow of being weighed along with the potash bulbs by being suspended from the hook of the balance.

These experiments perhaps throw some light on the cause of the losses of carbon dioxide and moisture experienced by the writer in using the wet method of combustion. Possibly these losses were caused by some stoppage in the apparatus or irregularity of gas flow. As a matter of fact the aspiration (which took place from beginning to end of the process) was made by a filter-pump which the writer has frequently observed does not exert an even and regular suction. Possibly all such losses are attributable (the drying and absorbing materials not being too long in use) to some such cause—perhaps a clogging up somewhere in the apparatus causing an irregular and jerky gas flow; or perhaps too much apparatus, causing, by its resistance, an uneven flow.

Dr. P. W. Shimer has greatly simplified the dry combustion apparatus and his apparatus will, without doubt, eventually altogether displace the old form. He also makes a notable change in the direction of greater simplicity—in the drying and purifying train. A train which vies with Shimer's for simplicity is that of Prof. Arnold's described in his book, "Steel Works Analysis," but in other respects there is a remarkable difference between the two. Shimer's train: cold water for HCl and Cl; calcium chloride for drying; Arnold's train: chromic acid solution for SO<sub>2</sub>; concentrated sulphuric acid for drying. It is seen that the difference is fundamental. The former is based upon the belief generally prevalent among American chemists that hydrochloric acid or chlorine, if present in the carbon sponge, is not absorbed by the copper oxide but passes out of the combustion tube, while sulphur dioxide is believed to be converted into sulphur trioxide in the pres-

ence of the glowing copper oxide and absorbed by it. Prof. Arnold's belief is the exact opposite of this; namely, that hydrochloric acid and chlorine are absorbed by the copper oxide of the combustion tube (p.40), and that sulphur dioxide escapes therefrom unchanged. Which theory is correct? That hydrochloric acid, if present in the carbon sponge, is not absorbed by the copper oxide, and does pass out of the combustion tube may easily be proved by testing the water of the Shimer absorption tube after a number of determinations have been made. On the other hand, as proof that sulphur dioxide passes out of the combustion tube, Arnold mentions an experiment in which potassium permanganate solution, placed after the combustion tube and connected with it, became decolorized by the gas. The writer finds that in using Arnold's chromic acid solution immediately following the combustion tube, as he directs, the chromic acid becomes entirely reduced, and the color of the solution changed to green after a considerable number of combustions have been made. But that this reduction is effected by hydrochloric acid,<sup>1</sup> and not by sulphur dioxide, is believed to be proved by the fact that when a bulb containing cold water is interposed between the combustion tube and the chromic acid bulb, the color of the chromic acid solution does not change; nor does the water of the bulb preceding show any trace of sulphur dioxide when tested with permanganate solution. If traces of the gas ever escape absorption by the copper oxide, Shimer's cold water tube would seem to be an ample safeguard. But as a further precaution, concentrated sulphuric acid, saturated with chromic acid, may be substituted for calcium chloride in the train.

The fact observed in the examination of Dougherty's method, of the carbon sponge being slightly soluble in hot nitric acid, suggested the suspicion that it might also be soluble in hot acid double chloride solution to some extent. The following tests were made on the same sample of steel:

Hot double  
chloride solution.  
Carbon. Per cent.  
1.052, 1.050, 1.06

Cold double  
chloride solution.  
Carbon. Per cent.  
1.076, 1.078, 1.077

In these tests the double chloride solution was heated (after

<sup>1</sup> Five drops (and probably less) of hydrochloric acid will completely reduce 10 cc. Arnold's chromic acid solution in the cold, standing over night.

solution of precipitated copper was nearly complete) for an hour or more, giving a much severer test of the solubility of the carbon than would occur in actual practice. It may therefore be inferred that the error from this cause in actual practice is very slight or in some cases nothing, for as the second result of the first table of results in this article shows that the carbonaceous residues from some steels are unacted on by hot nitric acid, so it is probable that such residues resist the slightly solvent action of hot double chloride solution. On the other hand, some residues may be much more soluble in hot double chloride solution than those of the above table. The point brought out by these results is merely that heating the double chloride solution of the drillings is attended with some risk of loss.

The carbon residue of the first table, that was not acted on by hot nitric acid was from a saw—a much-worked product. The carbon residues from such finished products seem different from those of ingot steels inasmuch as they give much darker shades to nitric acid in the color test than do the latter; thus, for instance, a 1.07 per cent. carbon steel in a finished saw gave 1.27 per cent. by the color test using a hammered slab as standard.

In washing the carbonaceous residue with hydrochloric acid it is perhaps safer to have the acid cold.

In carbon determinations, the error from moisture condensation in damp weather is well known. In a communication to the Society nearly two years ago the writer gave the results of experiments made in very damp weather which indicated the error from this cause to be usually 0.02 per cent. or 0.03 per cent., and occasionally as high as 0.05 and 0.06 per cent. When these experiments were made it was the writer's habit to have the balance-room door open; this door led into a small ante-room the door of which, at that time, also stood habitually open on account of warm weather, so that the outside air had access to the balance-room. For a long time back, however, the balance-room door has been kept closed, at least during the progress of combustions, and no such excessive condensation as 0.05 per cent. and 0.06 per cent. have occurred, using extra bulbs as an indicator. It is therefore believed to be well to keep the balance-room closed, at least in warm weather when adjoining parts of the laboratory are open. This is, of course, not an absolute

preventive. Moisture condensations equivalent to something under 0.02 per cent. carbon may easily occur.

#### THE COLOR METHOD.

The color method for high carbon steels is generally regarded with much distrust. Mr. Wm. Metcalf in his book, "Steel", says: "For in high carbons the color test in the best hands is only the wildest guess work." It is the writer's experience that the same drillings, even when dissolved at the same time, frequently do not give the same shade, and that by performing the test in the usual way, results as high as 0.10 per cent., or even higher, wide of the truth are often obtained. If the usual method be elaborated as follows, results not further from the truth than 0.03 per cent. (usually 0.01 or 0.02 per cent.), or at most 0.04 per cent. can uniformly be obtained: Duplicate tests of standard and samples are weighed out. Besides the standard, duplicate tests of two other steels in which the carbon has been accurately determined by combustion are also weighed out. In the absence of such steels, six samples of the standard are taken. When the color comparisons are made, the two steels of known carbon content are first tested, and from these tests is averaged a correction to be applied to all the results subsequently obtained. When these tests are finished the second sample of the standard is taken, the correction found as before, and the testing of the samples duplicated, and the average of these duplicates taken. These precautions are simple and obvious but are of no avail in the presence of a difficulty which, although it happens very rarely, still does happen. This difficulty is a carbon color showing a *much* deeper shade placed to the left of the standard than to the right of it, and requiring a further dilution equivalent to about 0.10 per cent. carbon to make the shade to coincide with the standard, the color when placed to the right showing no change by this dilution, and still agreeing with the standard. The result is then too high by just the amount represented by this extra dilution, or about 0.10 per cent., and it is necessary, therefore, when this abnormal shade is noticed, to discontinue the dilution and to take the reading when the color at the right coincides, ignoring the left-hand shade altogether.

No	As usual. Carbon. Per cent.	Left-hand shade ignored. Carbon. Per cent.	Combustion. Carbon. Per cent.
A4.....	$\begin{cases} 0.96 \\ 0.99 \\ 0.99 \end{cases}$	0.89	0.88
A6.....	$\begin{cases} 0.955 \\ 0.965 \end{cases}$	0.85	$\begin{cases} 0.85 \\ 0.85 \end{cases}$

LABORATORY OF HENRY DISSTON AND SON'S STEEL WORKS,  
PHILADELPHIA, PA.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL AND APPLIED  
CHEMISTRY, UNIVERSITY OF MICHIGAN.]

### A BURETTE FOR ACCURATE GAS ANALYSIS.

BY ALFRED H. WHITE.

Received April 27, 1900.

EVERYONE who has attempted to make accurate analyses of gases with the usual Hempel apparatus for technical gas analysis, knows there are many unavoidable sources of error, slight in themselves, but enough to make an exasperatingly large total at the end of a long analysis. The apparatus to be described was devised in the effort to eliminate some of these sources of inaccuracy. It is a modification of the Hempel burette with Petterson correction tube, the alterations being in the design of stop-cock and the position and form of the manometer, besides a change in the shape of the graduated tube to permit a more accurate reading of the gas volume. It has been used in its present form for the past year in this laboratory, and has been found to fulfil its purpose.

Some of the errors incident to analyses as usually conducted may be avoided by well-known precautions. If mercury instead of water is used as the liquid in the burette, errors due to solubility of the gas in the burette liquid and errors in reading due to water adhering to the walls of the burette, vanish. Errors due to solubility of gas in the reagent of the absorption pipette may be minimized by the use of a small quantity of the reagent in a pipette otherwise filled with mercury and may be greatly lessened when using an ordinary pipette by saturating the absorbing liquid with gas like that to be analyzed. Errors due to diffusion of gas through the liquid in the pipette are much more important than is usually believed, but may be obviated for most reagents by the use of a few cubic centimeters of mercury,

forming a trap at the bottom of the pipette. The errors which this paper aims to discuss and in part to remedy are those due to: Change in temperature and barometric pressure during an analysis; inclusion of air or leakage of gas while making connection with pipettes; and inaccuracy in reading gas volume.

Gas burettes in which the gas volume is unaffected by change of temperature and pressure have been devised and are well known. The Petterson correction tube as modified by Hempel, Drehschmidt, and others, consists of a glass tube of about the same dimensions as the burette, sealed at its lower end and with its upper end connected to one arm of a manometer whose other arm connects through a three-way stop-cock with the gas burette. This correction tube is enclosed in the same water-jacket as the burette, and hence the gas volume in it is affected by changes of temperature to just the same extent as the gas in the burette. When the liquid stands at the same height in both arms of the manometer, the pressure in the burette is the same as in the correction tube and therefore a constant, as the correction tube is sealed at its lower end. If the gas volume is read under these conditions it will be independent of changes in external temperature and pressure. There are several objections to the Hempel form of apparatus. The two rubber connections of the manometer may allow leakage of gas and consequent change in the supposedly constant pressure of the correction tube. Second, in drawing the gas out of the manometer into the burette there is a pronounced tendency on the part of the column of liquid to break when it starts down hill, especially at the rubber connection, with the result that some of it becomes carried into the burette with consequent change in the pressure indicated by the manometer. Figures 1 and 2 show the arrangement designed to overcome this difficulty. There is but one rubber connection in the manometer, and that is placed so that only mercury and never gas is brought in contact with it, thus rendering a leak with consequent change in pressure of the correction tube impossible. Communication with the manometer is established by turning stop-cock to position in Fig. 4. By placing the manometer below the stop-cock the further advantage is gained that in drawing the gas out of the manometer the mercury travels but a short distance and up hill only, meets with no bends

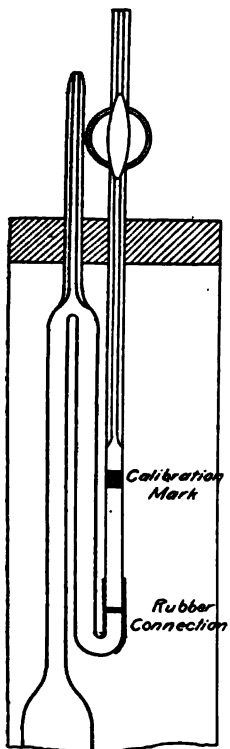


Fig. 1.

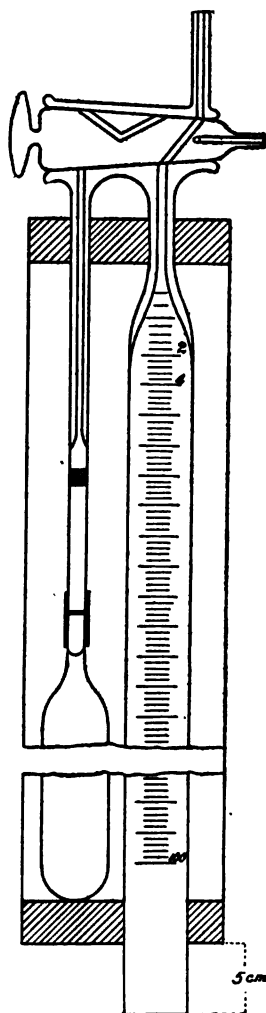


Fig. 2.

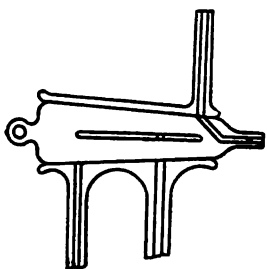


Fig. 3.

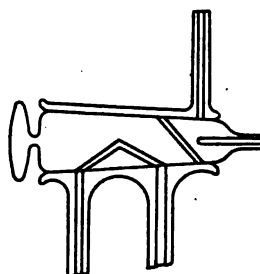


Fig. 4.

or inequalities in the tubing, and so may be drawn with great exactness to the stop-cock, drawing out all the gas without losing any of the mercury. The apparatus is all enclosed in the water-jacket and therefore all the same temperature, and is less cumbersome and apt to get broken than in other forms. The capillary tube projecting into the air behind the stop-cock as shown in Fig. 1 is to be sealed, under observed barometric pressure if desired, when the apparatus is first setup. The gas volume may be read when the mercury is at the same height in the two arms of the manometer and may then be reduced to standard conditions if desired. When this is not required, it is much more accurate to bring the mercury to a mark etched on the glass, or better tangent to the lower edge of a black metallic collar cemented around the manometer tube. In this case the gas will not be under the same pressure as that in the correction tube, but the variation will be a constant one and will cause no error. The connection between the burette and pipette is, as usual, made by a bent capillary tube and two rubber connections. Rubber connections, if properly made, introduce no appreciable error, but, because of their tendency to leak, form a serious menace to accuracy. Unfortunately no way has been found to dispense with them, and they are accepted by the author as a necessary evil. There is, however, an inherent source of error in the usual method of making the connection which the burette here presented completely obviates. With the apparatus ordinarily used, some of the gas under analysis will escape, or some unmeasured volume of air will be admitted to it whenever a connection is made. Perhaps usually both happen. The capillary tip of the burette, the connecting capillary, and the capillary tip of the absorption pipette, have a combined volume of about 0.5 cc. Although by various manipulative devices it is possible to restrict the error thus introduced from any individual operation to a fraction of this volume, it amounts in the course of a long analysis to a serious total. In the burette here presented it is completely eliminated.

By referring to Fig. 3, the stop-cock is shown turned in such a way that there is a clear passage from the capillary exit tube of the burette through the stop-cock to the outer air again. With the stop-cock in this position the pipette is to be connected



in the customary way to the burette but without any of the usual precautions to prevent inclusion of air. The liquid in the pipette is now blown up and through the capillary till it reaches the stop-cock. The capillary tube is thus completely filled with liquid. By turning the stop-cock to the position shown in Fig. 2 communication is established between the burette and pipette, and the gas may be passed over and absorbed as usual. After the absorption it is drawn over till the pipette-liquid just reaches the stop-cock, which is then turned back to the position in Fig. 3, allowing the liquid in the capillary of its own accord to siphon back into the pipette. The capillary is then to be rinsed out with a wash-bottle. In this way all the gas is each time drawn back into the burette for measurement. There is no gas lost in the capillary connecting tube, and no air is introduced, if the rubber connections have been properly made.

The gas volume in an ordinary gas burette may read with great accuracy with the assistance of a telescope, or some similar help, but it was desired to render such an adjunct unnecessary. The suggestion was taken from one of Bleier's<sup>1</sup> sketches. Fig. 5 shows schematically a gas burette with stop-cock and manometer as already described. The main body of the burette contains twelve bulbs, each of a capacity approximating 12 cc. A line is etched on each constriction and the capacity of the

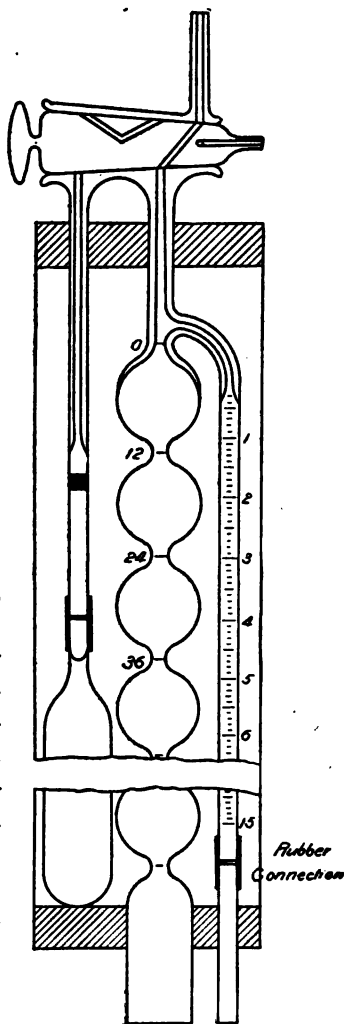


Fig. 5.

<sup>1</sup> C. Bleier, "Ueber gasometrische Apparate." *Ber. d. chem. Ges.*, 31, I, 238.

bulb between these marks is determined. Starting from the capillary above the top bulb a side arm springs, terminating in a small burette with total capacity of 15 cc. and graduated in 0.1 cc. Both these burette tubes connect at the bottom by means of heavy rubber tubes and a Y with a stop-cock on each arm, to a common leveling bottle. A screw clamp on each rubber tube serves for the exact adjustment of the mercury. To measure a gas, the stop-cock is placed in position in Fig. 3 and the mercury in the bulbed tube brought to the mark in one of the constricted portions by opening the proper stop-cock on the Y and raising or lowering the leveling bottle. When adjusted, the mercury is held in its proper position by closing the stop-cock on the Y. The stop-cock leading to the small burette tube is then opened and the gas brought to approximately atmospheric pressure by proper change in the mercury level. The three-way stop-cock at the top of the burette tube being now turned to position in Fig. 4, the burette is brought into connection with the manometer, which is properly set by further changing the level of the mercury in the small burette. The final adjustment in both burettes is made by the screw clamps on the rubber tubes. The volume of the gas will be read as  $x$  cc. in the bulbs +  $y$  cc. in side burette +  $z$  cc. in manometer. As there are these three readings to be made it is necessary that each be very accurate. Let us see how accurately this may be done. First, the mercury in the bulbed tube is to be brought to a specified mark in a tube of about 5 mm. internal diameter. By means of the screw clamp this may be done with such accuracy that the error is negligible. Second, the volume of gas in the side tube must be read. Each 0.1 cc. in this tube occupies a space of a little over 2.5 mm. and it is possible to interpolate 0.01 cc. with the eye with an error of less than 0.02 cc. Third, the mercury in the manometer must be brought to a definite mark with such exactness that the barometric pressure, under which the gas volume is read, shall be almost identical each time. A difference of 1 mm. of mercury pressure changes the gas volume 0.13 per cent., which on a volume of 100 cc. equals 0.13 cc., an error far too large. It was found impracticable to attain the required accuracy when it was attempted to bring the mercury to a mark etched on the glass. The best

device was found to be a band of thin, blackened copper, wrapped around the tube and cemented to the glass. It is possible to bring the mercury tangent to the lower surface of this with great exactness. In working with this burette the author is accustomed to make all readings in duplicate, readjusting at all points each time, and to repeat if the two differ from each other by more than 0.01 cc. Duplicates usually agree within this limit. The greatest difficulty found in manipulation is to draw the liquid from the pipette over exactly to the burette stop-cock and stop it there. If it gets into the burette, a bubble lodging in one of the capillary tubes frequently damps the sensitiveness of the manometer. If this happens the bubble may be shot out of its lodging place by compressing the rubber tube above the screw clamp. Such a bubble may also be carried into the manometer, where it will obscure the surface of the meniscus. To remedy this it is well to keep 2 or 3 mm. of water on the surface of the mercury in the manometer. This allows a perfectly sharp reading of the mercury meniscus below the water-level. The manometer should respond to a very slight movement of the screw clamp.

The advantages of this burette may be summarized as follows: It is a compact burette which, without reading-telescope or other accessories, allows the volume to be read with an error of less than 0.02 cc., compensates automatically for changes of temperature and pressure, and avoids completely all errors due to inclusion of air or loss of gas in making connections with the absorption pipettes. The disadvantages so far developed are chiefly those inherent in all forms of apparatus which possess a stop-cock and rubber connections. Both may leak; but on the other hand both may be kept so tight for limited periods of time as to introduce no measurable error.

Accurate apparatus is essential for accurate work and the author feels it but a just acknowledgment to thank Messrs. Greiner and Friedrichs for the care and skill with which they manufactured the burettes from his sketches.

ANN ARBOR, MICHIGAN,  
April, 1900.

## PREPARATION OF THE BLUE OXIDE OF MOLYBDENUM AND OF METALLIC MOLYBDENUM.

BY ALLEN ROGERS AND F. H. MITCHELL.

Received May 8, 1900.

BY the action of stannous chloride on an acid solution of a molybdate, a blue precipitate is produced. It was the investigation of this precipitate, that led to the following process: To prepare the blue precipitate, dissolve 50 grams of molybdenum trioxide in a sufficient quantity of ammonium hydroxide, to make a clear solution; to this add about the same quantity of water, make slightly acid with nitric acid, and then dilute with about five times its volume of water. To this solution add from 15 to 25 cc. of a 10 per cent. solution of stannous chloride. The very heavy precipitate which forms settles, and should be washed several times by siphoning off the supernatant liquid. These washings should be made as quickly as possible, as the blue precipitate becomes hydrated on standing, thus giving a deep blue solution.

After washing, the precipitate is thrown upon a plaited filter, and allowed to drain. It is then removed from the paper, while moist, into an evaporating dish, placed in the oven and dried at  $100^{\circ}$  C. This precipitate seems to correspond to the oxide of molybdenum,  $\text{Mo}_2\text{O}_3$ .

Place some of this oxide in a porcelain boat, and insert into an ignition tube, pass in hydrogen for a few minutes, then apply heat from a Bunsen burner for one hour, allow to cool, weigh and heat again for fifteen minutes, and continue heating until the weight is constant. The reduction takes from one hour to one and one-half hours, and may be hastened by moistening the oxide with a few drops of water. The molybdenum as prepared in this way is an ashen gray powder. The blue oxide is reduced more readily than the trioxide, under the same condition. In the electric furnace the blue oxide is rapidly reduced.

The accompanying figure illustrates a device by which we have been able to reduce various substances, and is very convenient in working with a small quantity.

The apparatus consists of a three-necked flask, A; the carbons, B and B', are held in position by asbestos plugs. B' has a

cavity in the end, into which the substance to be reduced is inserted. At C is an inlet and an outlet tube, by means of which an atmosphere of hydrogen is obtained. Fill the cavity

in B', remove the air, connect D and E with B and B', by means of copper foil, and having the proper resistance, turn on the current, and allow to pass until the desired effect is produced. The oxide was reduced in forty seconds, and, prepared in this way, resembles the product of the electric furnace; that is, a dull steel gray mass, which is very hard.

UNIVERSITY OF MAINE, ORONO, ME.

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### SOD OIL, WOOL GREASE, AND DEGRAS.

BY ERASTUS HOPKINS.

Received May 14, 1900.

**W**HEN the tariff act of 1897, known as the Dingley bill, was made a law to govern the classification of imported articles, there appeared a paragraph in the act which, with an intent of definite designation, opened a question which became so involved that its final settlement was made only after litigation.

The paragraph is No. 279, which reads "....; wool grease, including that known commercially as degreas or brown wool grease, one-half of one cent per pound."

The introduction of the term degreas caused all the trouble, because the authorities framing the bill did not make the fact clear that the term degreas is applied to oils and greases used by tanners without any special distinction.

For the question involved, research work was done in this laboratory on wool grease and sod oil, the results upon the latter being published in this Journal in 1899, p. 291.

As a result of the trial of the cases involved, sod oil was decided to be entitled to free entry as an oil used expressly for currying leather not specially provided for in the act, paragraph 568, and not similar to wool grease. Since that time I have been so often approached by people regarding the facts pertaining to the substances involved in the case that I thought the subject might be of wider interest than to the limited circle of my professional acquaintances.

Sod oil and wool grease have entirely different constitutions as well as characteristics, and hence should be easily distinguished apart.

I wish especially to call attention to the terms "wool grease," "degreas," and "sod oil."

Wool grease is extracted from the wool of sheep. Sod oil is expressed or extracted from leather which has been curried by oils, particularly fish oils.

Sod oil has no relation to wool grease in its derivation, but is related to it in its use; that is, for the currying of leather. Sod oil contains a resinous substance (not a resin) known as degreas former, which is characteristic of sod oil. No other oil or grease (and this includes wool grease, which is, scientifically speaking, an animal wax and not a grease at all) contains this degreas former, which is therefore characteristic of sod oil.

Originally, sod oil was called degreas. Later the term was made by the American oil trade and to a less extent by the English to embrace wool grease. The term degreas has therefore come to embrace two substances, dissimilar in constitution, source, and chemical constants. Wool grease being called degreas by the trade, caused the mention of degreas in paragraph 279 of

the act of 1897—a commercial term by which wool grease is known, as it is also known under the name of brown grease. The point I wish to make is that the *degras* there mentioned means wool grease but it does not embrace *sod oil* which in no way resembles it except in use. From this it can be seen that the term *degras* which originally had a limited meaning has come to be applied indiscriminately to the two substances used for currying and stuffing leather, and was mentioned in paragraph 279 to make that paragraph stronger in covering wool grease.

Paragraph 279 mentions two substances, tallow and wool grease. *Degras* is not mentioned in that paragraph excepting as a wool grease *degras*. Brown grease is mentioned also in this same connection.

Paragraph 568 mentions "all other greases and oils used for stuffing leather." Here also is included a *degras* but this *degras* is not that specially mentioned in paragraph 279 which is a wool grease, but is the original *degras*, or *sod oil* made from oil expressed from leather, and therefore having no connection with a wool grease which comes from wool. *Sod oil* is the English name for the substance known to the French as *degras* or *moëllon* and the term *degras* is the original French name for this oil extracted from oiled chamois leather and has been borrowed by the English to be misapplied to wool grease.

The term *sod oil* is unknown in the French currying trade excepting as an English translation of their own word *degras* or *moëllon*, and the process of making *degras* might be said to have originated in France in the manufacture of chamois leather.

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(CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.)

### A METHOD FOR THE DETERMINATION OF ZINC BY THE USE OF STANDARD THIOSULPHATE SOLUTION.<sup>1</sup>

BY RICHARD K. MEADE.

Received May 4, 1900.

AT the spring meeting of the Lehigh Valley Section, the author read a paper<sup>2</sup> upon a new volumetric method for magnesium. The method depended upon the precipitation of

<sup>1</sup> Read at a meeting of the Lehigh Valley Section, January 18, 1900.

<sup>2</sup> This Journal, 21, 746.

the magnesium as magnesium ammonium arsenate,  $\text{Mg}_3(\text{NH}_4)_2\text{As}_2\text{O}_7 + \text{H}_2\text{O}$ , and the determination of the arsenic in this precipitate by digestion with potassium iodide in a strongly acid solution, and titration of the liberated iodine with standard thiosulphate. When a solution of arsenic acid contains sufficient sulphuric or hydrochloric acid, the arsenic is quickly reduced by potassium iodide even in the cold from the higher to the lower state of oxidation. The reaction is expressed by the equation



Zinc is usually determined as a pyrophosphate by precipitation as zinc ammonium phosphate and ignition of this latter. Since the method above outlined for magnesium was suggested by the analogy between the phosphates and arsenates, the thought also occurred to me to make use of a volumetric method for determining zinc, somewhat similar to that for magnesium, by precipitating the zinc as an arsenate instead of a phosphate and determining the arsenic in the precipitate by titration with standard thiosulphate solution. From the equation given above and the formula for the zinc ammonium arsenate, each cubic centimeter of decinormal sodium thiosulphate should be equivalent to 0.00327 gram of zinc.

The method as tried for zinc was as follows: Pure zinc oxide,  $\text{ZnO}$ , was dissolved in dilute hydrochloric acid, an excess of ammonia added, and then 50 cc. of a 10 per cent. solution of sodium arsenate. The solution, after dilution to about 750 cc., was next warmed and nitric acid added until a slight turbidity was produced when the addition of nitric acid was discontinued and acetic acid added in its place, 1 cc. at a time, until the solution reacted acid to test paper. The precipitate was changed from curdy and flocculent to heavy and granular by heating and stirring. After allowing the precipitate to settle it was filtered off and washed. A hole was next punctured in the filter-paper, the zinc ammonium arsenate washed into a beaker, and 50 to 60 cc. of dilute hydrochloric acid added. The paper and the beaker in which the precipitate was formed were washed with the dilute acid until the solution and washings measured 85 to 100 cc. when from 2 to 3 grams of potassium iodide were added to the solution, and after allowing this latter to stand in



the cold a few minutes, the standard thiosulphate was run in from a burette until the color of the solution faded from red-brown to pale straw color and then, drop by drop, until all color vanished. The addition of starch for an indicator of the end of the reaction was found unnecessary in both the determination of magnesium and zinc by this method. Below are the results :

	Zinc oxide taken. Gram.	Equivalent in Zinc. Gram.	Zinc found. Gram.
1.....	0.2490	0.2000	0.1998
2.....	0.2490	0.2000	0.1994
3.....	0.2490	0.2000	0.2002
4.....	0.1245	0.1000	0.1004
5.....	0.1245	0.1000	0.1002
6.....	0.1245	0.1000	0.0998

Since calcium and magnesium are precipitated from alkaline solutions by sodium arsenate while zinc from an acid one, the successful attempt was made to separate the latter from the former two by first making the solution strongly ammoniacal, adding sodium arsenate, filtering off the calcium and magnesium arsenates, then making the solution acid with nitric and acetic acids and filtering off and determining the zinc as described above. The completeness of the separation is shown by these results.

Zinc oxide taken. Gram.	Equivalent in zinc. Gram.	Calcium carbonate added. Gram.	Magnesium oxide added. Gram.	Zinc oxide found. Gram.
0.2490	0.2000	0.2000	0.1000	0.1996
0.2490	0.2000	0.2000	0.1000	0.1992
0.2490	0.2000	0.2000	0.1000	0.2004
0.0623	0.0500	0.2000	0.2000	0.0500
0.0623	0.0500	0.2000	0.2000	0.0502
0.0623	0.0500	0.2000	0.2000	0.0496

Unfortunately manganese can not be so easily separated from zinc. In the case of ores, etc., it may, however, readily be gotten rid of by treatment with potassium chlorate and nitric acid after the solution of the ore.

The determination of zinc in a sample of ore was tried by first throwing down the manganese as a dioxide with potassium chlorate and nitric acid and filtering, separating the iron and alumina by double ammonia precipitations, then adding a large excess of sodium arsenate and filtering off the calcium and magnesium arsenates formed, and finally precipitating the zinc

by addition of nitric and acetic acids. The iodine liberated by digesting this precipitate in an acid solution of potassium iodide was then titrated with standard thiosulphate and the zinc calculated from the reading on the burette. The time required to run four determinations, without any effort at speed, was about eight hours.

The analysis of the ore by careful gravimetric methods was

	Per cent.
Zinc oxide.....	37.58
Manganese monoxide.....	15.33
Ferric oxide.....	29.69
Calcium oxide.....	1.12
Magnesium oxide.....	0.77
Silicon dioxide.....	12.77
Carbon dioxide.....	1.23
Water.....	0.76
	<hr/>
	99.25

Metallic zinc, 30.18 per cent.

By the volumetric method, outlined above, the results were

	Metallic zinc. Per cent.
1.....	30.00
2.....	29.98
3.....	30.04
4.....	29.98

LAFAYETTE COLLEGE, EASTON, PA.,  
January 18, 1900.

### NOTES.

#### *The Alleged Adulteration of Milk with Brain-matter.*<sup>1</sup>—

In the 1898 report of the Dairy Commissioner of the State of New Jersey, page 50, one of the chemists acting for the Commissioner, refers in rather intemperate language to the statements made in some text-books, concerning brain-pulp as a possible adulteration of milk and asserts that such adulteration has never occurred. He quotes the statement of König<sup>2</sup> to the effect that such addition to milk involves practical knowledge and resources which would hardly be possessed by milk-producers or purveyors, but Dr. König has not foreseen

<sup>1</sup> Read before the Philadelphia Section of the American Chemical Society, March 15, 1900.

<sup>2</sup> *Nahrungs- u. Genussmittel*, 2, 256.

the spread of education and the aid that such people may get from books and even from newspapers. We may, however, judge from König's statement that the German reports give no authentic instance of such addition, but we would be mistaken if we were to regard the allegation as on the same par with the popular fallacies about sand in sugar or chalk and water as a milk substitute. A consultation of trustworthy authorities will furnish some interesting data.

The earliest reference to the subject seems to have been in an anonymous article in the *Gazette d. Hôpitaux* (1841). Unfortunately the file of the *Gazette* at the College of Physicians lacks the numbers for 1841, but the general opinion of those who have consulted the article is that its statements are not worthy of credit. It appears to have been written in consequence of the agitation in France at that time over the enactment of laws regulating the sale of milk. The general subject of the composition of milk, its adulterations and the means of detecting them, had been discussed at great length by Quevenne in the *Ann. d. Hyg. Pub. et d. Med. Leg.* for 1841. In the same journal for 1842, many pages are given to the discussion of the adulteration of milk by brain-matter, the papers being by Quevenne and Gaultier de Claubry. A summary of the paper by the latter author is published in the *Bull. d. Acad. d. Med.*, 7 (1842). Quevenne regards the adulteration as unlikely, and thinks that it could not serve as a means of concealing added water but might be made to conceal skimming.

These French experimenters found that milk that had been adulterated by them with brain-matter presented properties different from those described by the anonymous writer in the *Gazette*.

A. H. Hassell, in his work on "Food Adulteration" (1876, p. 418) states that Mr. Queckett, the famous microscopist, exhibited drawings made from examinations of milk containing nerve tissue. It is further on record that Queckett stated before a committee of the House of Commons that he had found such structures in the sediment from a sample of milk examined about 1850, but had not observed it since. He submitted drawings of fields obtained from cows' milk with and without addition of calves' brains. As Queckett was an accomplished microscopist

and a scientific investigator, it does not seem likely that he would be mistaken on this point and he was evidently sure enough of it to make drawings of what he saw, and bring them to professional and official notice. We may, therefore, accept this record as one of trustworthy character. Hassell figures, on page 426 of the work above noted, a field showing the appearance of milk containing brain-matter, but does not state whether it is a copy of Queckett's drawings or from a sample prepared for the purpose.

Additional evidence as to this form of adulteration is presented in a communication by Sidney Gibbons, F. C. S., in the *Chemical News*, 33, 134 (1874). After a brief reference to the statements of Hassell and Queckett, Mr. Gibbons details an interesting experience of which the following is an abstract:

At a suburban hotel, near Melbourne, Victoria, frequent complaints had been made of the quality of the milk supplied, and on a certain date a sample was furnished to the chemist. As received, the sample had formed into three layers, the highest and lowest being thick and dirty gray, the middle one thin and colorless. When shaken, the mass became uniform and pulpy without frothing but stratified again on standing. Its specific gravity was 1022. The top layer did not closely resemble cream and contained but few fat-cells. The lowest stratum was darker, including dirt, sand, and vegetable matter. Much granular and clotted matter was present which was distinguished from fat by staining with magenta. There was no material amount of starch, though a few granules were present. Many peculiar cell-structures resembling brain-cells were seen under the microscope. Mr. Gibbons mixed some sheep's brain with milk and obtained optical appearances similar to those in the sample. He did not succeed, however, in making so smooth a mixture, possibly because the milkman had manipulated the material more elaborately. The fields observed agreed closely with the drawings given by Hassell.

From these reports it seems justifiable to record brain-matter, especially calves' and sheep's brains, as adulterations of milk that have occurred and may again occur, and therefore not to be overlooked in the analytic manuals.

Quevenne and Gibbons incline to the view that this form of adulteration is not dangerous to the public health, although, of course, not in any sense permissible. Such views may be easily excused when we consider how little was known, even at the date of Gibbons' report, concerning the diseases likely to be conveyed by milk. The view of the French and English chemists is based on the fact that brain-matter is a regular article of food but this loses its value when we remember that for such purpose the brains are cooked, which would be rarely the case when used for milk adulteration. Apart from the liability of the brain to contain virulent microbes, the localization there of certain stages of dangerous entozoa is by no means infrequent.

It is a question whether some of the special milk-laws would cover this form of adulteration but it is clearly prohibited by the general food-law in operation in most of the states of the United States, and butter made from such milk would come under the provisions of the national and state laws concerning oleomargarin.

It seems to me that this form of adulteration might easily escape notice. Brain-matter may give a rich creamy color to skimmed milk. All those who have written about the subject have spoken of the use of the microscope for detecting the adulterations, but in the routine inspection of milk-supplies, microscopic examination is rarely employed, and hence the adulteration might be overlooked. I have prepared samples by adding to skimmed milk, some calves' brain well pulped and strained through a close-mesh sieve. The nerve tissue can easily be seen with a moderate magnifying power. Evaporation in a milk-dish does not show anything different from ordinary milk, but the odor emitted when the residue is charred, preparatory to taking the ash, is suggestive of foreign animal matter. When the sample was treated with the mixture of pentyl-alcohol and hydrochloric acid, and then with strong sulphuric acid in the usual manner for rapid fat-determination, no peculiar reactions were noted. The proteids dissolved quite as readily in the acid as that from pure milk. The brain-pulp was found to be rapidly soluble without striking color in cold strong sulphuric acid.

HENRY LEFFMANN.

*A New Form of Receiver for Fractional Distillation in Vacuo.*<sup>1</sup>—

While there are several forms of receivers which give satisfaction, when small quantities of liquids are fractionated *in vacuo*, most of them are open to the serious objection that it is necessary to destroy the vacuum to change receivers or to remove all or part of the distillate; these difficulties are entirely obviated by the apparatus shown in the figure.

The receiver consists of three separatory funnels sealed together, each of the three bulbs being provided with a side stop-cock, the uppermost having an additional one, which is connected with the vacuum pump.

The condenser tube enters into the top bulb, connection being made by a ground glass joint, for which a rubber stopper may be substituted if desired.

The *modus operandi* is obvious and almost automatic; the stop-cocks *a*, *d*, *e*, and *f* are closed, *b*, *c*, and *g* opened, the last being connected with the vacuum pump; the first fraction is collected in bulb A, the stop-cock *b* closed, and the second fraction collected in bulb B; by closing stop-cock *c*, the third fraction may be collected in bulb C.

If it is desirable to separate the distillate into more than three fractions, or if the quantity of the distillate exceeds the capacity of the bulbs (which may be 1 liter each), the apparatus shows its special advantages.

Suppose the first fraction has been collected in bulb A and the second is being received in B; by opening stop-cock *d*, air is admitted into A, and the contents withdrawn through *a*; closing this and connecting *d* with a second pump, the vacuum is re-established in A. This point may be ascertained without the aid of a separate manometer by slightly opening *b* when, if the vacuum is less in A than in B, air will bubble through the liquid in the latter, while if the pressure in both bulbs is the same, or if it is less in A, the distillate will flow down to A, where it may be collected and drawn off as before, and the operation repeated *ad infinitum*.

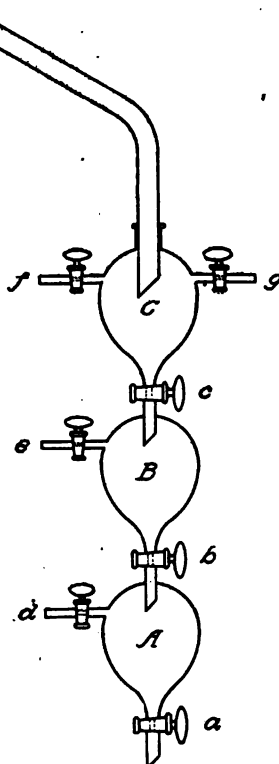
With a little experience a receiver of a total capacity of three liters may be so manipulated as to distil several liters of liquid without interruption. In actual practice 40 liters are

<sup>1</sup> Read at the meeting of the Cincinnati Section, February 15, 1900.

regularly distilled in this way, and each fraction is made sharp and exact, as there is no disturbance of the vacuum.

With bulbs of smaller capacity, *e. g.*, 250 cc. each, it is unnecessary to employ more than one pump, since the vacuum will not appreciably diminish in the short time necessary to close *g*, disconnect the pump, attach it to *d*, and reestablish the vacuum in this bulb. A makeshift apparatus, embodying the principles of the one shown in the sketch, can be made in any well-equipped laboratory by connecting three separatory funnels by means of two-holed rubber stoppers, the other holes being occupied by bent glass tubes provided with stop-cocks or even rubber tubing and pinch-cocks.

For continued use the apparatus with the bulbs sealed together is to be recommended; the one described has been used almost daily by the writer and was made according to his designs by E. Greiner, No. 62 Centre Street, New York.



LUCIEN FOGETTI.

#### OBITUARY.

Hon. Nathaniel Peter Hill, of Denver, Colorado, scientific metallurgist, sometime professor of chemistry in Brown University, and later United States Senator from Colorado, was born in Montgomery, N. Y., February 18, 1832; he died in Denver, Colorado, May 22, 1900.

His father and mother were notable people in Orange County, N. Y. The father, a well-to-do and substantial farmer, had been lieutenant of cavalry in the war of 1812 and subsequently he held many offices of trust in his county where he was

respected as a man of superior abilities and high character.

When Senator Hill entered Brown University in the year 1853 he was a bright and promising young man, matured and developed by the responsibility which had come upon him, while yet little more than a boy, of managing the farm after his father's death. His interest in scientific agriculture led him to devote his chief attention to chemistry, and his progress in the subject was so rapid and so substantial that he was soon made an instructor, and in 1859, he was appointed professor of chemistry. He soon set about the securing of funds for a new chemical laboratory for the university, and he accomplished the work of its construction in 1862.

A little later his attention was directed to the freshly opened gold-bearing districts in Colorado. The field appeared so promising that in 1864 he resigned his professor's chair and turned his attention to practical metallurgy. He was early impressed with the necessity of *smelting* rather than *milling* the Colorado ores of Gilpin County, and he proceeded to make a careful study of the whole subject at the metallurgical works of Freiberg, in Saxony, and Swansea, in Wales. As a result, he formed a business connection with the noted house of Vivian & Sons in Swansea. In 1867 he organized the Boston and Colorado Smelting Co., a concern which has operated successfully for over 30 years and of which up to the time of his death he was the general manager. Professor Hill is acknowledged as the chief agent in the creation of that great industry which was necessary to the development of the mineral resources of his adopted State.

Space does not permit a full statement here of his achievements, but a partial enumeration of his official and business positions speaks volumes. He was mayor of Black Hawk, Colorado, in 1871; member of the Colorado Territorial Council, 1872-3; United States Senator from Colorado, 1879-1885; member of the International Monetary Commission, 1891; president of the United Oil Company, working in the Florence district; president of the Colorado Smelting and Mining Company, operating on an extensive scale in Montana; president of the Denargo Land



Company, engaged in developing real estate in the vicinity of Denver; principal owner of the *Denver Republican*.

As a chemist and scientific man Professor Hill was characterized by clear insight, great grasp of his subject, and sound judgment. His scientific work related chiefly to applied chemistry. During his professorship in Brown University he continually acted as expert and adviser in connection with chemical manufacturing establishments in and near Providence. But his life-work was in metallurgy, and the complex operations of his refining establishments near Denver are a monument to his power in the scientific treatment of metallic ores. As a university professor he was highly valued; he was not only recognized as a master of his subject and as a clear thinker, but more, he was loved by his pupils as a true gentleman. He was a remarkably able business man, having far-sightedness, wisdom, and courage. As a legislator he secured—as he merited it—a reputation for ability, dignity, and integrity.

Professor Hill married Miss Alice Hale, of Providence, R. I., a member of a remarkably able New England family, and a woman of superior powers and great sweetness of character. She survives him with three children: Crawford Hill (A. B., Brown University, 1885), Miss Isabel Hill, and Mrs. Gertrude (Hill) Berger.

J. H. APPLETON.

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### NEW BOOKS.

ANALYSE ÉLECTROCHIMIQUE. PAR EDGAR F. SMITH, Professeur de Chimie à l'Université de Pennsylvanie. Traduction par Joseph Rosset, Ingénieur civil des Mines. Paris: Gauthier-Villars. 1900.

The hearty favor with which this excellent little work was received on its first appearance by English-speaking chemists, and its translation into the two languages that can boast of more voluminous electrochemical literatures than the English, are doubtless sources of much gratification to its author. This French version, like the German that preceded it, is a clear and faithful translation of the second American edition of 1894. It contains a few changes and additions such as the separation of some of the platinum metals, analytical results, and some useful tables, yet these are hardly of sufficient importance to justify the

translator's claim "c'est donc en quelque sorte une édition originale paraissant en français que nous présentons." As a feature quite unusual in French books of this kind, we note that careful attention has been given to the spelling of the names of foreign authors.

H. F. KELLER.

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#### ERRATUM.

On page 139, line 10, of February, 1900, issue, for the formula " $[(CH_3)_3NH]_2TeCl_4$ ," substitute " $[(CH_3)_3NH]_2TeCl_6$ ."

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

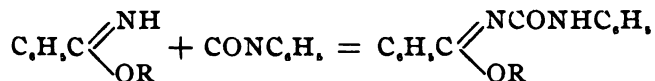
[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

### ON UREAIMIDO ESTERS, THIOUREAIMIDO ESTERS, ACYL- THIOUREAIMIDO ESTERS, AND UREAAMIDINES.

[PRELIMINARY PAPER.]

BY HENRY L. WHEELER AND W. MURRAY SANDERS.

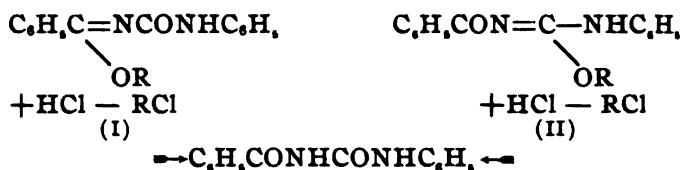
REPRESENTATIVES of new classes of compounds, isomeric or metameric with the acylpseudourea ethers, acylpseudothiurea ethers and diacylpseudothiurea ethers, can be prepared by combining isocyanates, mustard oils, and acyl rhodanides with imido esters. The imido esters immediately combine with phenyl isocyanate, at ordinary temperatures, giving a quantitative yield of an addition product as follows:



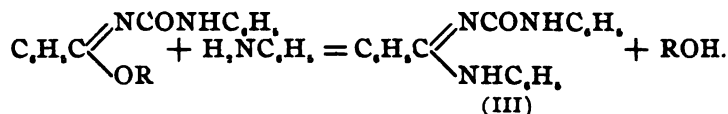
This class of compounds, perhaps, may be called urea-imido esters or carbamidimido esters, since they have the structure of imido esters and ureas combined. They are extremely sensitive towards hydrogen chloride by which reagent, just as the acylpseudourea ethers<sup>1</sup> (II) they are readily and quantitatively converted in the cold, with loss of alkyl chloride, into acylureas.

<sup>1</sup> Stieglitz and Dains: This Journal, 21, 136.

This reaction with these two classes of compounds proceeds as follows:

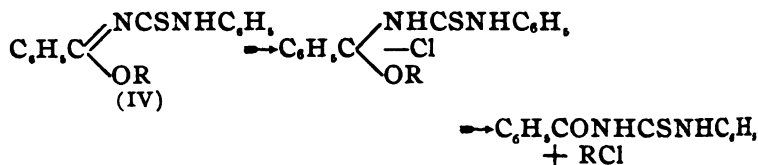


It will be noticed that the imido ester grouping in the different positions in these isomers are affected alike, inasmuch as under similar conditions both compounds give with hydrogen chloride the same derivative, benzoylphenylurea. The ureaimido esters (I) readily react with aniline, at the temperature of the steam-bath, and ureaamidines are formed as follows:



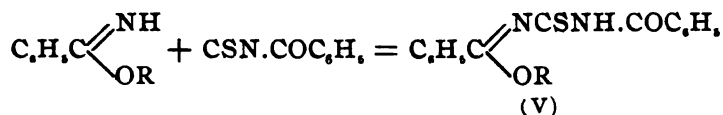
Whether the structure shown in formula (III) or the tautomeric form is to be assigned to these amidines must be decided later. These amidines have little or no basic properties.

The mustard oils, phenylmustard oil and allyl mustard oil, react less energetically than phenyl isocyanate with the imido esters. On long standing or on warming, the mixtures deposit crystals. These compounds, for which the name thioureaimido esters (IV) is proposed, are closely similar to the above oxygen analogues, since with hydrogen chloride, under similar conditions, they readily separate alkyl chloride and give the corresponding acylthio ureas. The mechanism of the reaction is as follows:

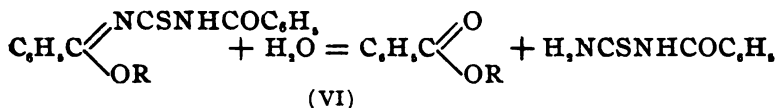


The isomeric acylpseudothiourea ethers and the diacylpseudothiourea ethers apparently have not yet been prepared, so that a comparison of the behavior of these compounds with the thioureaimido ester derivatives must be deferred to a later date.

When the thioureaaimido esters are warmed with aniline, and other organic bases, thioureaaimidines are formed. Like the above ureaaimidines they appear to have no basic properties. The fact that they are not soluble in alkali affords new evidence that the double union of the imido ester grouping confers a basic nature to the molecules. Here, however, it is neutralized by the negative character of the urea group. The imido esters combine with acetyl and benzoyl thiocyanates with evolution of heat, the mixtures readily solidifying. Acylthioureaaimido esters (V) are then produced, as follows:



These compounds are formed more readily than the above and they are far more unstable than the thioureaaimido esters. When they are warmed with hydrochloric acid they decompose in a different manner from the other types of ureaaimido esters. A monoacylthiourea, and not a diacyl derivative, is obtained. The decomposition under this treatment takes place at the double union as follows:



What appears to be the nearest known analogue to a metamer of the above or dibenzoylpseudothiurea ether is the ethylisodiacarbethoxyurea,  $\text{C}_6\text{H}_5\text{O.CON}=\text{C} \begin{array}{l} \text{NCO.OCC}_6\text{H}_5 \\ \diagup \\ \text{OCC}_6\text{H}_5 \end{array}$ , of Dains.<sup>1</sup> This

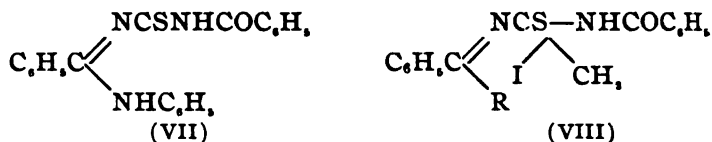
compound is also very sensitive towards hydrogen chloride; however, it does not separate at the double union, like the above, but decomposes with the evolution of ethyl chloride, giving the diacylurea,  $\text{C}_6\text{H}_5\text{O.CONHCONHCO.OCC}_6\text{H}_5$ . The ease with which the ureaaimido esters decompose with hydrochloric acid, without forming a stable intermediate addition product or "salt," recalls the perfectly analogous behavior of the acylimido esters.<sup>2</sup> In the case of the latter, the above two reactions with

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Wheeler, Walden and Metcalf: *Am. Chem. J.*, 19, 129 and 20, 64.

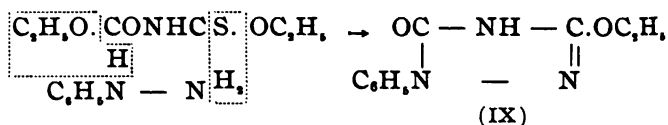
hydrogen chloride were also observed. The properties of the ureaimido esters, in general, approach more nearly to those of the acylimidoesters than to those of other types of imido esters.

When the acylthioureaaimido esters are treated with aniline, toluidine, etc., acylthioureaamidines (VII) are formed in the normal manner. These compounds, as well as the thioureaaimido esters, combine with alkyl halides, the addition probably taking place to the sulphur as shown in formula (VIII).



The action of phenylhydrazine on the acylthioureaaimido esters seemed theoretically promising for the preparation of triazole derivatives; but it appears, from preliminary experiments, that, although hydrogen sulphide is evolved in this treatment, triazoles do not result, at least not as the chief product. The hydrogen sulphide, first formed, decomposes a part of the ureaimido ester, giving benzoylthiourea, etc.

Experiments in this laboratory by Dr. Bayard Barnes have shown that the acylphenylthioureas react with aniline and phenylhydrazine with the removal of the acyl group. With phenylhydrazine no triazole derivative was obtained. Similar results were obtained with the acylphenylurethanes, acetylphenylurethane, formylphenylurethane<sup>1</sup> and acetylphenylthiourethane. It is probable that other diacylanilides will be found to act similarly. On the other hand those acylurethanes which do not contain a phenyl group such as acetylurethane,<sup>2</sup> acetyl- and benzoylthionurethane, give triazole derivatives. Dr. Barnes has also found that carbethoxythionurethane of Delitsch<sup>3</sup> readily reacts with phenylhydrazine as follows :



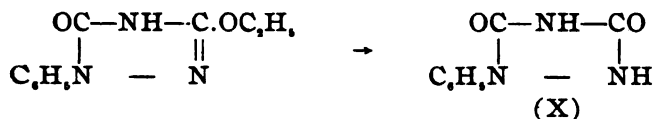
That the compound formed in this reaction is 1-phenyl-3-

<sup>1</sup> Wheeler and Metcalf: *Am. Chem. J.*, 19, 217.

<sup>2</sup> Andreocci: *Ber. d. chem. Ges.*, 22, R. 737; *Ibid.*, 24, R., 203.

<sup>3</sup> *J. prakt. Chem.*, 10, 118.

ethoxy-5-triazolon, and that it has the structure represented by formula (IX), is shown by its behavior, on boiling with strong hydrochloric acid, whereupon it is converted into Pinner's urazole, (X):



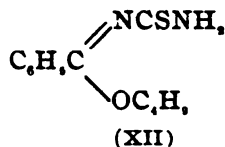
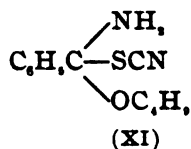
The process which in general serves for the preparation of simple or monosubstituted ureas and thioureas, and which consists of treating a salt of an amine with potassium cyanate or thiocyanate, does not lead to the formation of the prototypes of the above urea derivatives, when applied to the salts of the imido esters. This fact seems to the writer to be a strong argument in support of the theory of Stieglitz that the salts of the imido esters are not ammonium derivatives, but that they are derived

from the form  $\text{RC} \begin{array}{l} \nearrow \text{NH}_2 \\ \text{---} \text{Cl} \\ \searrow \text{OR} \end{array}$ , etc. In fact, the properties of the cyanic

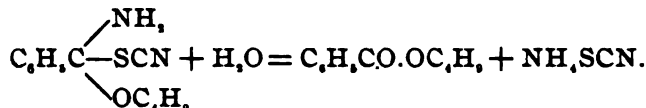
and thiocyanic acid salts do not agree with those which would be expected for salts having an ammonium structure.

When ice-cold solutions of benzimidobutyl ester hydrochloride and potassium cyanate, in molecular proportions, are mixed together, a mass of well-crystallized, colorless prisms separate. If an attempt is made to filter these at ordinary temperature they rapidly decompose, giving off a gas ( $\text{CO}_2$ ?), and completely liquefying. Owing to the unstable nature of this salt, which is undoubtedly a cyanate, it was not examined further. On the other hand, the corresponding thiocyanic salt is far more stable. It can be prepared, at ordinary temperature, by mixing solutions of the imido ester hydrochloride with potassium thiocyanate, whereupon a bulky mass of colorless prisms or needles separate. This salt has the structure represented by formula (XI), and all attempts to rearrange it into the metameric thioureaimido ester (XII) failed.

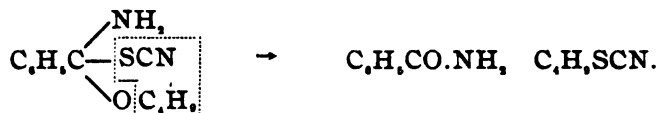
<sup>1</sup> *Ber. d. chem. Ges.*, 21, 1219.



When this salt is warmed in aqueous solution it dissolves, but the solution almost immediately becomes turbid and an oil (isobutyl benzoate) separates. On evaporating to dryness nothing but ammonium thiocyanate is obtained. The decomposition then proceeds as follows :



If the dry salt is heated above its melting-point it decomposes smoothly as follows :



It will be noticed that these reactions are analogous in every respect to those of the hydrochloric acid salts of the imido esters.

#### EXPERIMENTAL PART.



Phenyl isocyanate (3.4 grams) and benzimidoisobutyl ester (10 grams) combined with evolution of heat and the mixture solidified to a white mass. When this was crystallized from alcohol, colorless prisms were obtained which melted from 99°-100°. A nitrogen determination gave :

	Calculated for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$	Found.
Nitrogen.....	9.4	9.1

*Action with Hydrogen Chloride.*—Some of the above material was dissolved in benzene and the solution was saturated with hydrogen chloride whereupon colorless prisms separated, melting at about 200°. This material proved to be *Benzoylphenylurea*,  $\text{C}_6\text{H}_5\text{CONHCONHC}_6\text{H}_5$ , which crystallized from alcohol in long



silky needles, and on boiling it with sodium hydroxide it gave phenylurea.

The extreme sensitiveness of compounds of this type towards hydrochloric acid was shown by the fact that it was found to be impossible to isolate ureaimido esters from benzimidomethyl, ethyl, and phenylacetimidomethyl esters and phenyl isocyanate, if the latter contained phosphorus oxychloride. Under these conditions the benzimido esters gave *benzoylphenylurea*, while phenylacetimidomethyl ester gave a compound very difficultly soluble in alcohol. It crystallized in the form of needles and melted at 166° and a nitrogen determination showed that it was *phenylacetylphenylurea*,  $C_6H_5CH_2CONHCONHC_6H_5$ :

	Calculated for $C_{18}H_{14}N_2O_2$	Found.
Nitrogen.....	11.0	11.0

*Action with Aniline.*—Phenylureaimidoisobutyl benzoate (2 grams) and aniline (0.6 gram), were mixed in benzene and warmed on the water-bath whereupon a substance separated in granular crystals. It was found to be very difficultly soluble in alcohol (a property of ureaamidines, which is general as far as we have observed, and on boiling with alcohol it melted from 179°–180°. A nitrogen determination agreed with the figures calculated for *benzenylphenylureaphenylamidine*,  $C_6H_5NH-(C_6H_5)C=NCONHC_6H_5$ .

	Calculated for $C_{19}H_{17}N_3O$	Found.
Nitrogen.....	13.3	13.0

This amidine is insoluble in dilute hydrochloric acid and no hydrochloric acid salt was obtained when the material was dissolved in benzene and saturated with hydrogen chloride. It is insoluble in alkali.



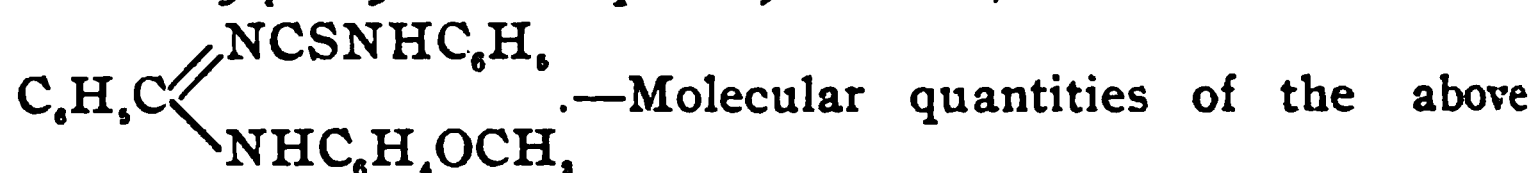
Equal quantities of benzimidomethyl ester and phenyl mustard oil (5 grams of each) were mixed and kept at a temperature of about 60°–70° for two days. On cooling, then, the mixture solidified almost completely. In each of the experiments with phenyl mustard oil and the imido esters, a yellow mixture resulted although the ingredients before mixing were colorless.

On crystallizing from alcohol beautiful colorless or cream-colored lozenge-shaped tables were obtained which melted sharply at  $132^{\circ}$ . The material is readily soluble in benzene and hot alcohol, difficultly in cold alcohol, and a nitrogen determination gave:

	Calculated for $C_{18}H_{14}N_2OS.$	Found.
Nitrogen.....	10.37	10.29

When this compound was treated with cold dilute hydrochloric acid, in which it is insoluble, little or no action was observed after two days' standing. When a little alcohol was added and the whole was warmed, effervescence took place, methyl chloride was evolved, and, on cooling, the long characteristic colorless needles of *benzoylphenylthiourea*,  $C_6H_5CONHCSNHC_6H_5$ , were obtained, melting about  $148^{\circ}$ .

*Benzenylphenylthiourea-p-anisylamidine*,



imido ester and *p*-anisidine were mixed in benzene solution and allowed to stand at a temperature of about  $70^{\circ}$  for several hours, whereupon a mass of plates or scales separated. This material was very difficultly soluble in alcohol and in benzene. When crystallized from these solvents and from amyl acetate, it melted at about  $180^{\circ}$ . A satisfactory nitrogen determination was not obtained, undoubtedly owing to the fact that this substance, as well as the corresponding phenyl and naphthyl amidines, burn with great difficulty, the results invariably coming low.



Benzimidoethylester (5 grams) and phenyl mustard oil (4.5 grams) gave a yellow oil directly on mixing. After two days the material solidified to a glistening mass of flattened prisms or tables and on crystallizing from alcohol it separated in the form of cream-colored tables and it melted sharply at  $119^{\circ}$ . These thiourea-imido esters, in general, show a great tendency to crystallize. A nitrogen determination gave:

	Calculated for $C_{16}H_{16}N_2OS.$	Found.
Nitrogen.....	9.8	9.7

When treated with hydrochloric acid it behaved precisely like the methyl ester and benzoylphenylthiourea was obtained.

*Phenylthiourea isobutyl Benzoate*,  $C_6H_5C \begin{matrix} \nearrow NCSNHC_6H_5 \\ \searrow OC_6H_5 \end{matrix}$ .—Benz-

imidoisobutyl ester (5 grams) and phenyl mustard oil (3.8 grams) behaved, on mixing and standing, precisely like the above. When crystallized from alcohol it forms large, stout tables and it melts at  $125^\circ$ . A nitrogen determination gave:

	Calculated for $C_{18}H_{20}N_2OS$ .	Found.
Nitrogen.....	8.9	8.9

When this was treated with hydrochloric acid and warmed, *benzoylphenylthiourea* was obtained.

When 2 grams of this imido ester were warmed on the water-bath with aqueous-alcoholic ammonia for a number of hours and then allowed to cool, colorless crystals separated melting from  $151^\circ$ – $153^\circ$ . A nitrogen determination gave 18.5 per cent., while the calculated for benzenylphenylthiourea amidine is 27.0 per cent., and that for phenylthiourea which melts at  $154^\circ$  is 18.4 per cent. The material, in fact, had the bitter taste and other properties of *phenylthiourea*.

When this thioureaimido ester was treated with methyl iodide a varnish was obtained which crystallized after long standing.

Phenylthiourea isobutyl benzoate readily reacts with phenyl hydrazine, giving off hydrogen sulphide and it gives a compound which crystallizes in plates when treated with benzoyl chloride. These reactions will receive more thorough attention later.

*Benzenylphenylthiourea phenylamidine*,  $C_6H_5C \begin{matrix} \nearrow NCSNHC_6H_5 \\ \searrow NHC_6H_5 \end{matrix}$ .—

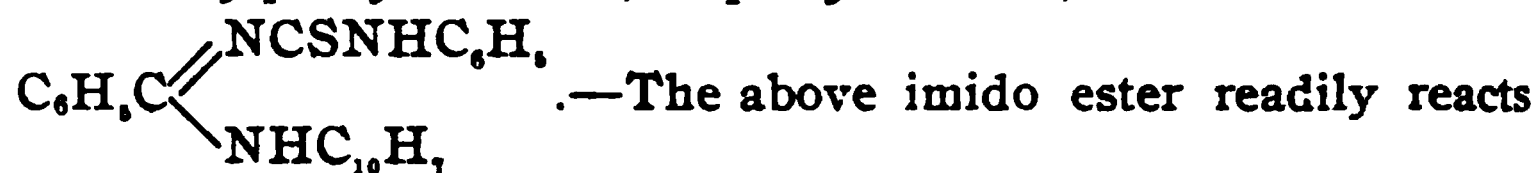
The above imido ester (4 grams) and aniline (1.1 grams) after warming on the water-bath gave off only a trace of hydrogen sulphide. The product, on crystallizing from alcohol, formed a beautiful mass of large thin plates. They melted from  $151^\circ$ – $152^\circ$  and a nitrogen determination gave:

	Calculated for $C_{20}H_{17}N_3S$ .	Found.
Nitrogen.....	12.6	12.0

This material is insoluble in cold hydrochloric acid, concen-

trated or dilute. On warming, it dissolves, but on cooling it crystallizes out again unaltered. Platinum chloride precipitates a curdy yellow mass from the concentrated hydrochloric acid solution.

*Benzenylphenylthiourea-β-naphthylamidine*,



with β-naphthylamine, giving a compound that crystallizes in minute plates and which is extremely insoluble in the ordinary organic solvents; when crystallized from alcohol and amyl acetate it melted, not sharply, from 182°–183°. The material burned very slowly and a satisfactory nitrogen determination was not obtained, the calculated being 11.0 per cent. while 10.0 was found.

*Acetylthiourea imidoisobutyl Benzoate*,  $\text{C}_6\text{H}_5\text{C} \begin{array}{l} \nearrow \text{NCSNHCOCH}_3 \\ \searrow \text{OC}_3\text{H}_7 \end{array}$

—Benzimidoisobutyl ester and acetyl thiocyanate combine with evolution of considerable heat and, on cooling, the mixture completely solidifies, whereupon, on crystallizing from alcohol, colorless needles are obtained which melt from 125°–126°. A nitrogen determination gave:

	Calculated for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$ .	Found
Nitrogen.....	10.0	9.9

When this imido ester was treated in alcoholic solution with hydrogen chloride a compound was obtained melting at 166° and which had all the properties of *acetylthiourea*,  $\text{CH}_3\text{CONHCSNH}_2$ .

With phenylhydrazine it evolves hydrogen sulphide, and on crystallizing the product from alcohol acetylthiourea separates.

*Benzoylthiourea imidoethyl Benzoate*,  $\text{C}_6\text{H}_5\text{C} \begin{array}{l} \nearrow \text{NCSNHCOC}_6\text{H}_5 \\ \searrow \text{OC}_2\text{H}_5 \end{array}$

—When benzimidoethyl ester (6.1 grams) was mixed with 5.6 grams of benzoyl sulphocyanate the mixture completely solidified. On crystallizing from alcohol, needles were obtained which melted from 131°–132°, and on analysis the following result was obtained:

	Calculated for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ .	Found.
Nitrogen .....	8.9	8.8

When this imido ester was warmed with phenylhydrazine the only crystalline material obtained was *benzoylthiourea*.



—When benzimidoisobutyl ester (10 grams) and benzoyl sulphocyanate (7.4 grams) were mixed, considerable heat was evolved and the mass solidified. When this was crystallized from alcohol, colorless needles, melting at  $120^\circ$  were obtained. A nitrogen determination gave:

	Calculated for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$ .	Found.
Nitrogen .....	8.2	8.4

When this imido ester was treated with hydrogen chloride in benzene solution, *benzoylthiourea*, melting at  $169^\circ$ – $170^\circ$  was obtained. Apparently this same compound was obtained when the ester was treated with ammonia, phenylhydrazine and with benzoyl chloride. These results show the great tendency this ester has to separate at the double bond.

*Benzoylthiourea*imidoisobutyl Benzoate Methyl Iodide,



—The above imido ester and methyl iodide combine in benzene solution to form a compound containing iodine and which crystallizes from alcohol in well-developed, colorless prisms melting from  $204^\circ$ – $205^\circ$ . A nitrogen determination gave:

	Calculated for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_3\text{SI}$ .	Found.
Nitrogen .....	5.7	5.7



—When molecular proportions of the above imido ester and aniline were heated in benzene solution a substance was obtained which crystallized in colorless prisms and which melted from  $145^\circ$ – $146^\circ$ . A nitrogen determination gave:

	Calculated for $\text{C}_{21}\text{H}_{17}\text{N}_3\text{OS}$ .	Found.
Nitrogen .....	11.6	11.2

No hydrochloric acid salt was obtained when this amidine was treated with hydrogen chloride.

*Benzenylbenzoylthioureaorthotolylamidine,*

$$\text{C}_6\text{H}_5\text{C} \begin{array}{l} \nearrow \text{NCSNHCOCH}_3 \\ \searrow \text{NHC}_6\text{H}_4\text{CH}_3 \end{array}$$
 .—This compound was obtained on fusing the imido ester with ortho toluidine. It crystallized from alcohol in colorless prisms which melted from 116°–117° and a nitrogen determination gave :

	Calculated for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{OS}$ .	Found.
Nitrogen.....	11.2	10.8

*Benzoylthioureaimidomethylphenyl Acetate,*

$$\text{C}_6\text{H}_5\text{CH}_2\text{C} \begin{array}{l} \nearrow \text{NCSNHCOCH}_3 \\ \searrow \text{OCH}_3 \end{array}$$
 .—When phenylacetimidomethyl ester (5.6 grams) was treated with benzoylthiocyanate (5 grams), the mixture solidified immediately. It was crystallized from alcohol and obtained in the form of colorless needles melting from 116°–117°. A nitrogen determination gave :

	Calculated for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ .	Found.
Nitrogen .....	8.9	9.3

When this imido ester was treated with phenylhydrazine, hydrogen sulphide was evolved but the product, on crystallizing from alcohol, was neither an amidine or a triazole. It contained 15.4 per cent. of nitrogen while the calculated for *benzoylthiourea* is 15.5 per cent. It agreed in all its properties with the acylthiourea.

*Benzoylthioureaimidoethylphenyl Acetate,*

$$\text{C}_6\text{H}_5\text{CH}_2\text{C} \begin{array}{l} \nearrow \text{NCSNHCOCH}_3 \\ \searrow \text{OC}_2\text{H}_5 \end{array}$$
 , was prepared from phenylacetimidoethyl ester. It forms colorless needles from alcohol which melt from 140°–141°. When treated with hydrogen chloride in alcoholic solution it gave small prismatic crystals, melting from 169°–170°, and a nitrogen determination agreed with the calculated for benzoylthiourea :

	Calculated for $\text{C}_9\text{H}_9\text{N}_2\text{SO}$ .	Found.
Nitrogen .....	15.5	15.6

*The Thiocyanic Acid Salt of Benzimidoisobutyl Ester,*

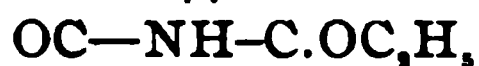
$$\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{C}_6\text{H}_5\text{C} - \text{SCN} \\ \diagdown \\ \text{OC}_2\text{H}_5 \end{array}$$
 is readily formed on mixing aqueous solutions of the imido ester hydrochloride and potassium cyanate. It then separates as a mass of colorless needles or prisms which are quite difficultly soluble in water. It melts at about  $130^\circ$ . A portion dried in a desiccator over calcium chloride and then for a few minutes at  $60^\circ$ – $70^\circ$  gave the following results on analysis:

	Calculated for $\text{C}_{11}\text{H}_{16}\text{N}_2\text{SO}$ .	Found.
Nitrogen.....	11.8	11.9

Its reaction with iron chloride and with alkali showed that this material was a salt of the imido ester and not the isomeric thioureaaimidoisobutyl benzoate. It decomposes on warming with water smoothly into ammonium thiocyanate and isobutyl benzoate and when heated above its melting-point it gives benzamide and isobutyl thiocyanate.

## EXPERIMENTS BY BAYARD BARNES.

*Carbethoxythioncarbamic Ester*,  $\text{C}_6\text{H}_5\text{OCONHCS}.\text{OC}_2\text{H}_5$ .—This was prepared according to the directions of Delitsch;<sup>1</sup> when purified by means of its potassium salt, it was found to boil unaltered at  $135^\circ$  at 13 mm. pressure. It melts at  $44^\circ$ .



*1-Phenyl-3-ethoxy-5-triazolone*,  $\text{C}_6\text{H}_5\text{N}-\text{N}=\text{N}$ , was obtained when the above carbamic ester (15 grams) was heated with phenylhydrazine (9 grams) on the steam-bath. After the evolution of hydrogen sulphide and alcohol had ceased, the material was crystallized from hot water, whereupon colorless needles, melting from  $150^\circ$ – $151^\circ$ , were obtained. This material was soluble in alkali and was precipitated unaltered by acids. It contained no sulphur and on analysis the following results were obtained:

	Calculated for $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_2$ .	Found.
Carbon .....	58.5	58.9
Hydrogen .....	5.2	5.3
Nitrogen .....	20.5	20.4

<sup>1</sup> *J. prakt. Chem.*, 10, 118.

When this compound was boiled for some time with concentrated hydrochloric acid and alcohol, colorless plates were obtained, which melted at  $263^{\circ}$ , showing signs of melting at  $255^{\circ}$ . For purposes of comparison Pinner's<sup>1</sup> urazole was prepared and it was found to be identical with the above.

*Acetylphenylurethane*,  $\text{CH}_3\text{CO}(\text{C}_6\text{H}_5)\text{NCO}.\text{OC}_6\text{H}_5$ .—Ten grams of phenylurethane were boiled with an equal weight of acetic anhydride for several hours whereupon, on pouring into water, unaltered urethane was obtained. Acetyl chloride was then added and boiled for about one hour. Then about one-half of the solution was distilled off at ordinary pressure and the remainder at 10 mm. pressure whereupon the material practically all boiled from  $142^{\circ}$ – $143^{\circ}$ . It was thus obtained as a colorless oil which, like formylphenylurethane, refused to solidify on cooling. A nitrogen determination gave :

	Calculated for $\text{C}_{11}\text{H}_{13}\text{NO}_3$ .	Found,
Nitrogen.....	6.7	7.3

When this compound was gently warmed with phenylhydrazine and the product was crystallized from benzene, colorless plates, melting at  $128^{\circ}$ , were obtained. The following nitrogen determination showed that this material was not a triazole derivative but rather *acetylphenylhydrazine* :

	Calculated for $\text{C}_8\text{H}_{10}\text{N}_2\text{O}$ .	Found.
Nitrogen.....	18.6	18.0

The action of phenylhydrazine on Hegershoff's<sup>2</sup> *acetylphenylthiocarbamide*,  $\text{CH}_3\text{CONHCSNHC}_6\text{H}_5$ , melting at  $139^{\circ}$ , although some hydrogen sulphide was evolved, did not lead to the formation of a triazole derivative, at least not as the chief product. The material that separated, on crystallizing from alcohol, formed large, four-sided plates melting at  $153^{\circ}$  and having all the properties of *phenylthiourea*. In other words the action of phenylhydrazine, in this case, removes the acetyl group.

NEW HAVEN, CONN., May 29, 1900.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Ber. d. chem. Ges.*, 32, 3658.



# THE NUCLEIC ACID OF THE EMBRYO OF WHEAT AND ITS PROTEIN COMPOUNDS.<sup>1</sup>

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received June 16, 1900.

Frankfurt<sup>2</sup> has estimated the proportion of various constituents of the embryo of wheat and found globulin, 21.62 per cent., and albumose, 13.62 per cent.

O'Brien<sup>3</sup> states that the proteids of wheat germs consist of globulins of the myosin-type, coagulating at 55°, soluble in dilute solutions of sodium chloride or magnesium sulphate and precipitated by excess of these salts; globulins of the vitellin type, coagulating at 75°–78° and soluble in dilute solution of sodium chloride, but not precipitated by an excess; proteose; and albumin not coagulating below 80°, soluble in sodium chloride solution, not precipitated by an excess, nor by dialysis, nor by carbonic acid.

As neither of these investigators has given more than a superficial account of the protein<sup>4</sup> substances found by him in the embryo of wheat, we determined to investigate this subject, in order to learn definitely which of the proteins contained in the wheat kernel are predominant in the embryo, and whether there is any special difference in character between the proteins of the more physiologically active germ and those of the dormant endosperm.

As a result of this investigation we have found that, of the proteids described by one of us<sup>5</sup> as constituents of the wheat kernel, the albumin (leucosin), the globulin, and the proteose, which in the whole seed are present in small proportions, together constitute a large part of the embryo, and further, that gliadin and glutenin, the principal proteid constituents of the endosperm, are not present in the embryo.

<sup>1</sup> From advance sheets of the Report of the Connecticut Agricultural Experiment Station for 1899, communicated by the authors.

<sup>2</sup> *Versuchs-Stationen*, 47, 449.

<sup>3</sup> *Annals of Botany*, 9, 543.

<sup>4</sup> In this paper the term protein denotes the basic molecules which, combined with simple acids, form the "simple proteids," and combined with other more complex groups, form the "compound proteids" (Hammarsten, "Text-book of Physiology," translated by Mandel, third edition (1900.) The term proteid in this paper includes both of these groups of protein compounds.

<sup>5</sup> Osborne and Voorhees: *Am. Chem. J.*, 15; 392 (1893).

Although the globulin and leucosin obtained from the whole seed were free from phosphorus, all of our preparations of the globulin, and many of those of the albumin, from the embryo contained various yet considerable quantities of this element, and when digested with pepsin, yielded insoluble products having the characteristics of nuclein. The elementary composition of those preparations of the embryo-albumin which contained no phosphorus, or only traces, was the same as that of leucosin prepared from the whole seed, while the composition of those embryo-albumin preparations which contained phosphorus differed from that of leucosin in proportion to the phosphorus present.

Analyses of different preparations of embryo-globulin showed no agreement, even when corrected for ash.

These facts led us to examine our extracts for nucleic acid, and having found this acid and determined its composition, it was seen that the differences just alluded to disappear if we assume the phosphorus to be present as nucleic acid and calculate the analyses free from this acid and from ash.

In a paper recently published by one of us on "Some Definite Compounds of Protein Bodies"<sup>1</sup> it was shown that many, if not most preparations of so-called native proteids are, in fact, compounds of protein bodies with acids, and it was suggested that nuclealbumins might prove to be similar phosphoric acid compounds.

In that paper it was also shown that the crystallized globulin, edestin, obtained from hemp-seed, forms a compound with one, and another compound with two molecules of hydrochloric acid, both of which are crystalline, and that the preparations of this globulin as commonly obtained are mixtures of these in various proportions. It was also shown that the protein molecule can combine with more than two molecules of acid, so that several multiple compounds of one acid with the same protein molecule can undoubtedly exist.

That our preparations from the wheat-embryo are mixtures of two or more compounds is shown by the variable proportions of phosphorus which they contain. That phosphorus is a chief factor in determining the proportion of nuclein that separates

<sup>1</sup> This Journal, 21, 486.

during pepsin digestion is shown by the fact that the amount of nuclein found is always in close relation to the amount of phosphorus contained in the preparation.

That the preparations are not mixtures of already formed nuclein with ordinary proteid matter is shown by the difference in solubility and behavior of the original preparation from that of the nuclein derived from it.

It would seem, then, that the nuclein obtained by pepsin digestion is not an original constituent of the extract nor of the cells of the embryo, but results through combination of several molecules of nucleic acid with one of protein.

Accordingly we conclude that these phosphorus-containing preparations from the wheat embryo are mixtures of different protein nucleates and that when subjected to pepsin digestion, in consequence of the conversion of a part of the protein substance into proteose, the proportion of nucleic acid to unaltered protein is increased, so that higher acid nucleates are formed which are insoluble in the digestive fluid.

The grounds for these conclusions are given in the following detailed account of our investigation.

The material at our command consisted of a quantity of wheat germs, a specially prepared product of the Pillsbury Mills, from which the bran and endosperm had been thoroughly removed, which was kindly procured for us by Mr. David Chidlow, of Chicago.

The germ meal, which was prepared and sent to us in cold weather, was immediately extracted with petroleum naphtha and ground to a flour.

#### I. The Nucleic Acid of the Wheat Embryo.

We shall later show that the precipitate produced by saturating the slightly acid aqueous extract of this wheat-embryo meal with sodium chloride contains almost all the phosphorus of the extract. We accordingly extracted a large quantity of the meal with water, saturated the extract with sodium chloride and subjected the precipitate to a vigorous pepsin digestion. We thus obtained a considerable quantity of nuclein from which we prepared nucleic acid in the following manner:

The nuclein was thoroughly washed with water and then

dilute potash solution was added until all the nuclein had dissolved and its solution become faintly alkaline to phenolphthalein.

This solution was cautiously treated with dilute hydrochloric acid until a precipitate was formed, which separated readily from the solution. This was filtered out and the clear filtrate found to yield no precipitate on adding a *little* more acid. A considerable quantity of strong hydrochloric acid was then added, causing a precipitate of nucleic acid, which separated in large flocks that rapidly settled to a coherent layer. The deposit continued to contract and soon became so dense and brittle that it could be ground to a powder even under water. The solution was decanted, the sediment was thoroughly washed, redissolved with alkali and again thrown down by adding acid. Since this last precipitate still contained much coloring-matter, it was again dissolved with alkali and the solution poured into alcohol. This retained the basic coloring-matter and threw down a voluminous precipitate of potassium nucleate, which was thoroughly washed with large quantities of alcohol, dried to remove the alcohol and then dissolved in water and the nucleic acid reprecipitated by an excess of hydrochloric acid. Since all the coloring-matter had not been removed by the preceding treatment, the precipitate was twice dissolved in alkali and precipitated by pouring into a large volume of alcohol. The nucleic acid was then thrown down by gradually adding dilute hydrochloric acid to the solution of the potash salt; after thoroughly washing the precipitated acid with water and with alcohol it was dried over sulphuric acid and found to weigh 10.14 grams.

After drying to constant weight in hydrogen at 100°, its weight remained unchanged on further heating at 110° in air. When thus dried it had the following composition :

	I.	II.
Carbon.....	36.18	36.31
Hydrogen.....	4.48	4.42
Nitrogen.....	16.03	16.10
Phosphorus .....	8.95	8.86
Ash .....	3.52	....
P <sub>2</sub> O <sub>5</sub> in ash.....	2.88	....
Difference .....	0.64	....

The ash consisted, chiefly if not wholly, of potassium meta-

phosphate and therefore by subtracting from it the phosphorus pentoxide which it contained, we obtain the amount of inorganic base which had been precipitated as an acid salt together with the free nucleic acid. Calculating our analyses free from this base, we have the following figures :

## COMPOSITION OF NUCLEIC ACID.

	Calculated for $C_{21}H_{21}N_8P_2O_{18}$ .	Found.
Carbon.....	36.16	36.48
Hydrogen.....	4.45	4.48
Nitrogen.....	16.01	16.17
Phosphorus.....	8.89	8.96
Oxygen.....	34.49	33.91
	<hr/> 100.00	<hr/> 100.00

About 2 grams of this preparation were hydrolyzed by heating for an hour and a half in a boiling water-bath with 2 per cent. hydrochloric acid.

On adding ammonia to this solution, a precipitate soon separated which was digested on the water-bath with an excess of ammonia, filtered out, washed, dried over sulphuric acid, and found to weigh 0.27 gram.

This substance gave the murexide reaction and was insoluble in hot ammonia, both of which properties are characteristic of guanin. On analysis this crude guanin was found to contain :

	Calculated for guanin $C_5H_5N_5O$ .	Found.
Carbon.....	39.74	40.96
Hydrogen.....	3.31	3.67
Nitrogen.....	46.36	45.21
Oxygen.....	10.59	10.16
	<hr/> 100.00	<hr/> 100.00

The solution filtered from the guanin was precipitated by cold ammoniacal silver nitrate and the voluminous, gelatinous precipitate washed, pressed on filter-paper, suspended in water, and decomposed by hydrochloric acid. The solution containing the hydrochloride of another base, was repeatedly evaporated with water to decompose the chloride and the free base found to weigh 0.2272 gram. This was again dissolved in water and the silver salt precipitated from a boiling solution, the silver compound

was decomposed with hydrochloric acid, and the solution of the hydrochloride was evaporated and crystallized.

The substance separated wholly in four-sided prisms, most of which were truncated by planes at right angles.

This hydrochloride was then converted into the picrate by dissolving in water, adding a little ammonia, evaporating to dryness, dissolving in about 100 cc. of water, and precipitating with a 1.1 per cent. solution of picric acid added cautiously. The very voluminous yellow precipitate was quickly filtered out with the help of a pump, washed thoroughly with water, and dried over sulphuric acid. We thus obtained 0.3766 gram of a picrate, which lost nothing on drying at  $110^{\circ}$  and had the following composition:

	Calculated for adenin picrate, $C_{11}H_8N_8O_7$ .	Found.
Carbon.....	36.27	36.07
Hydrogen.....	2.19	2.51
Nitrogen.....	30.77	30.28
Oxygen.....	30.77	31.14
	<hr/> 100.00	<hr/> 100.00

From the behavior of this base and the composition of its picrate, it is evidently adenin. Since this acid yields on hydrolysis the purin bases, guanin and adenin, as well as phosphoric acid, there can be no doubt that it is a true nucleic acid closely related to the guanylic acid recently described by Bang.<sup>1</sup> The facts that we obtained these two bases from the nucleic acid in nearly molecular proportion and that almost all the nitrogen of the acid was recovered in the guanin and adenin separated from it, lead us to believe that both these bases exist together in the acid molecule. If such is the case, our formula already given must be multiplied by 2.5, making it  $C_{28}H_{22}N_{20}P_5O_{25}$ . This formula resembles that of guanylic acid, which, calculated to the same basis, is  $C_{28}H_{22}N_{20}P_5O_{25}$ . The two acids are different, since Bang's guanylic acid yields a pentose on hydrolysis, whereas we have obtained no evidence that any sugar can be derived from our acid. As we are at present engaged in a study of the reactions and constitution of this acid, we will reserve further statements respecting it for a future paper, which we expect to be able to publish soon.

<sup>1</sup> *Ztschr. phys. Chem.*, 26, 133.

## II. The Proteids of the Wheat Embryo.

## THE AQUEOUS EXTRACT.

The germ flour, described on page 381, when treated with water, yields a gummy mass from which a clear extract is secured with difficulty. From 500 grams of meal an extract was obtained with 2,000 cc. of water, of which 1,400 cc. could be filtered clear. This extract was neutral to litmus, alkaline to lacmoid, and so acid to phenolphthalein that 19 cc. of decinormal alkali were required to neutralize 100 cc. of it to this indicator.

When a freshly prepared, dilute, aqueous extract of the recently ground wheat germs is heated in a water-bath, no coagulation occurs, the solution becoming slightly opalescent. If a more concentrated extract, such as may be obtained by treating 1 part of meal with 5 parts of water is thus heated, the entire solution solidifies to a firm, opaque jelly, free from visible particles. If to either of these solutions a very little hydrochloric acid is added before heating, an abundant flocculent coagulum separates on heating.

After standing awhile, the aqueous extract becomes gradually acid to limus, so that when heated slowly it becomes turbid at about 50° and a large flocculent coagulum separates at 55°. Heated to 65° for some time and filtered, a second coagulum may be obtained on raising the heat from 65° to 100°. The amount of this second coagulum is about one-third that of the first.

The coagulated proteid is dissolved by 0.5 per cent. potassium hydroxide solution, but not perceptibly by 0.4 per cent. hydrochloric acid solution, unless the latter is heated, when a clear transparent jelly is formed.

Freed from coagulable protein, the aqueous extract still contains a relatively large amount of substance which has the reactions of proteose.

When the concentrated aqueous extract is poured into a large volume of distilled water, a turbidity forms at first, which mostly disappears after shaking, indicating the absence of a notable quantity of globulin held in solution by the salts dissolved from the meal.

Saturation of the extracts with sodium chloride gives a considerable precipitate, only a small part of which can be redis-

solved in dilute salt solution. When this dissolved part is precipitated by again saturating with salt, it also is converted, to a large extent, into an insoluble form; the part still remaining in solution is, like a globulin, precipitated by dialysis.

When the solution saturated with sodium chloride is filtered, and the diluted filtrate saturated with ammonium sulphate, a part of the precipitate produced, when redissolved in water, is thrown out of solution by saturating with sodium chloride, though before precipitation with ammonium sulphate it dissolved in saturated sodium chloride solution.

These reactions show that changes occur which involve the albumin coagulating at  $55^{\circ}$ , for after freeing the extract from all protein precipitable by saturating with salt or by dialysis, there remains in solution only a small proportion of this albumin.

Thus, an aqueous extract corresponding to 666 grams of germ meal, when heated to  $65^{\circ}$ , yielded 62 grams of coagulum, or 9.3 per cent.; a similar extract on dialysis deposited 9.2 per cent., only 0.87 per cent. of coagulable and 2.0 per cent. of uncoagulable protein remaining in solution. The precipitate, produced by dialysis, was but slightly soluble in salt solution, having become largely coagulated. From these facts it is clear that one and the same protein substance gives rise to these apparently different protein bodies, and consequently the substance which O'Brien considered to be a globulin of the myosin type and an albumin, coagulating at  $80^{\circ}$ , are in fact derivatives of the same protein substance.

The cause of these changes was not determined, though it seems most probable that they are the result of a slow development of acid in the extract, which, by uniting to the protein in increasing proportions, forms chemically different substances. Such a development of acid takes place rapidly in muscle plasma, under the influence of which quite similar changes in the proteins there present can be observed.

Why Frankfurt overlooked albumin, present in such large proportion in the aqueous extract, is not easily understood, unless, before heating his solutions, he either added no acid or too much, so that he converted this substance into an uncoagulable acid compound.

Hydrochloric acid added to the extract in very small quantity



causes a flocculent coagulum to separate on heating, while a slightly larger quantity, added before heating, entirely prevents the formation of this coagulum. Acetic acid and nitric acid give precipitates in the extracts which are not soluble in a reasonable excess of either of these acids.

In order to determine definitely the relations of these variously obtained substances, we have made a large number of fractional precipitations under quite different conditions, an account of which we now give:

An extract was made by treating 700 grams of germ meal with seven times its weight of water, straining through bolting-cloth and filtering the liquid perfectly clear. This was slightly colored, perfectly neutral to litmus, alkaline to lacmoid, and strongly acid to phenolphthalein. A portion of it was at once heated for one hour in a water-bath at 60°, and the large coagulum produced was filtered out, washed thoroughly with hot water and with alcohol and dried over sulphuric acid, giving 24 grams of preparation 1.

Another preparation was made by heating in a water-bath at 65°, 2,000 cc. of a clear aqueous extract, obtained by treating 3,000 grams of the germ meal with 9,000 cc. of water. The coagulum produced, when washed with hot water and alcohol and dried over sulphuric acid, weighed 62 grams, forming more than 9 per cent. of the oil-free germ meal. This is preparation 2.

Another aqueous extract was heated at 65°, until all the proteid coagulable at this temperature had separated. The coagulum produced, when washed with hot water and alcohol was dried over sulphuric acid and found to weigh 16.68 grams. The filtrate from this coagulum, heated in a boiling water-bath, yielded a second coagulum which, when washed and dried, formed preparation 3, weighing 4.9 grams.

A portion of the extract, which yielded preparation 1, was saturated with ammonium sulphate; the resulting precipitate was dissolved as far as possible in water, its solution filtered clear, and dialyzed for four days. During this time a considerable precipitate formed, that, when filtered out, was found to be insoluble in salt solution. The solution, filtered from that substance and dialyzed in running water until nothing more sepa-

rated, was filtered and heated at 60°, which caused a coagulum. This coagulum, washed with hot water and with alcohol and dried over sulphuric acid, weighed 7.1 grams and made preparation 4.

In a clear water extract of wheat germ meal, dialyzed four days, there appeared a dense turbidity, due apparently to a globulin, since it dissolved on adding sodium chloride. Passing carbon dioxide gas through the dialyzing solution seemed to increase the turbidity, but effected no definite separation. As it was found that 10 cc. of N/10 hydrochloric acid per 100 cc. of the extract caused a separable precipitate, this proportion was added and the resulting flocculent precipitate brought into solution again by adding salt. The clear extract was then dialyzed for two days in running water and filtered from an amorphous precipitate, which was treated as later described on p. 400.

The filtrate from this precipitate was further dialyzed for three days more in running water and then, as nothing separated, for four days more into alcohol. The precipitate which resulted was dried over sulphuric acid, exhausted with water, in order to remove all uncoagulated proteids, as well as other soluble substances, dehydrated with absolute alcohol, again dried and weighed, yielding 12 grams of preparation 5.

Another aqueous extract was saturated with pure sodium chloride, the abundant precipitate filtered out, treated with dilute brine and the resulting solution filtered from a relatively considerable quantity of insoluble matter. This filtrate was saturated with sodium chloride, a second precipitate filtered out and likewise treated with dilute salt solution. The insoluble portion was removed by filtration and the clear filtrate dialyzed. The small precipitate separated by dialysis was washed and dried, weighed 4.8 grams, and formed preparation 6.

The filtrate from the first precipitation of the substance of preparation 6, caused by saturating its solution with sodium chloride, as described above, was diluted with water and saturated with ammonium sulphate. The precipitate which resulted was dissolved in water and its solution precipitated by saturating with sodium chloride. Although this substance had previously been soluble in saturated brine, after precipitation with ammonium sulphate it was found to be nearly all insoluble

therein, so that almost complete precipitation resulted on again saturating with sodium chloride. The precipitate so produced was filtered out, dissolved in dilute salt solution, and reprecipitated by dialysis. We thus secured 7.6 grams of preparation 7.

By saturating another aqueous extract of germ meal with sodium chloride a very large quantity of proteid was separated which was filtered out, exhausted with dilute salt solution and washed thoroughly with water and alcohol. Dried over sulphuric acid, the preparation, 8, weighed 17 grams.

The filtrate and saline washings from preparation 8 were united and again saturated with salt, and yielded a small precipitate which, dissolved in brine and precipitated by dialysis, gave preparation 9, weighing 2.8 grams. As the salt-saturated solution from which this preparation had separated contained so little protein, it appears that nearly all the proteid precipitated from the aqueous extract by saturating with salt had been converted into the insoluble substance forming preparation 8.

The filtrate, from the salt-saturation precipitate produced in the aqueous extract, was dialyzed in water for several days and the still clear solution then dialyzed in alcohol for twenty-four hours. The proteid, thereby precipitated in a coagulated state, was filtered out, washed with water and then with alcohol, yielding 12.4 grams of preparation 10.

Another aqueous extract was saturated with sodium chloride and the precipitate, treated in the same way as preparation 8, yielded 18 grams of preparation 11.

The saline washings of the last preparation were dialyzed free from chlorides and gave a precipitate weighing 2.86 grams when washed and dried, which formed preparation 12, having the properties of a globulin, dissolving readily on adding salt and being precipitated from such solution by water.

The filtrate from the final precipitation of 12, when heated in a boiling water-bath, gave a coagulum which formed preparation 13, weighing 1.64 grams.

The salt-saturated filtrate from the first precipitation of 11, as already described, was heated to boiling and the coagulum produced was filtered out, giving preparation 14, weighing 5.47 grams.

Since analysis showed that most of the preparations already

described contained phosphorus, some even in large amount, we made an attempt to separate the phosphorus from our extract, in order to determine, if possible, the relation of the preparations free from phosphorus to those which contained much phosphorus.

Two thousand grams of meal were treated with 6 liters of distilled water and the extract (4 liters) was squeezed out as completely as possible in a press.

As a preliminary experiment, 100 cc. of this clear, filtered extract were made faintly alkaline to phenolphthalein, with about 40 cc. of N/10 potassium hydroxide solution. To insure a sufficient quantity, 20 cc. more of alkali were added and thereupon a little calcium chloride, which gave a precipitate that seemed to partly dissolve on adding sodium chloride. The undissolved part, when washed with dilute salt solution, water, and alcohol and dried, weighed 1.7 per cent. of the meal, contained about 55 per cent. of organic matter, and left 45 per cent. of ash, consisting of tricalcium phosphate.

To 2,000 cc. of the original extract were then added 1,350 cc. of a solution containing alkali equivalent to 1,560 cc. N/10 solution, with sodium chloride enough to form 6.5 per cent. of the total liquid. To this, a solution of calcium chloride was added, as long as a precipitate formed, and after standing over night the solution was decanted from the precipitate and filtered clear on a pulp filter. Of the clear filtrate, 2,200 cc. were made as neutral as possible to *litmus*, by adding 180 cc. of N/10 hydrochloric acid solution. Of the thus neutralized solution, 1,000 cc., when gradually heated in a water-bath, became turbid at 52° and a considerable coagulum separated at 53°. After the temperature had been slowly raised to 65° and kept at this point for some time, the coagulum was filtered out, washed and dried as usual, giving preparation 15, weighing 6.4 grams. Another portion of this extract, filtered from the calcium chloride precipitate, was saturated with ammonium sulphate while still slightly alkaline to litmus, the resulting precipitate filtered out, dissolved in water, its solution filtered clear and dialyzed. A slight precipitate formed on dialysis, which was removed by filtering, the solution was heated in a boiling water-bath and the proteid thus coagulated was filtered out, washed, dried, and weighed as usual, giving 3.07 grams of preparation 17.

To determine what effect the removal of the phosphorized substance thrown out by calcium chloride had upon precipitation with salt, we made neutral to litmus a liter of the filtrate from the calcium chloride precipitate and then saturated with sodium chloride. The large precipitate which formed was washed by decantation with water, in which it gradually dissolved, until only an insignificant quantity remained. The similarly obtained precipitate from the simple aqueous extract we have shown on page 389, to be nearly all insoluble in water.

To separate globulin from the aqueous extract, 1,200 cc. of clear, filtered extract were obtained from 200 grams of the germ meal treated with 2,000 cc. of water. One liter of this extract was dialyzed in running water for six days, and the large precipitate resulting filtered out, washed with water and alcohol, and dried over sulphuric acid, giving preparation 18, weighing 9.17 grams.

These preparations, thus variously obtained from the aqueous extract, were dried to constant weight at 110° and analyzed with the following results, most of the figures given in the table being the average of closely agreeing duplicate determinations:

TABLE I.—COMPOSITION OF PREPARATIONS OF PROTEID FROM THE WATER EXTRACT OF THE WHEAT EMBRYO.

	1	2	3	4	5	6	7	8	9
Carbon.....	51.13	50.52	50.17	52.39	51.77	52.13	52.73	43.59	52.28
Hydrogen..	6.85	6.81	7.01	6.83	6.81	7.04	7.11	5.77	6.97
Nitrogen...	16.28	16.47	16.66	16.20	16.11	16.48	16.00	15.16	16.38
Sulphur....	1.18	1.17	1.00	1.32	1.30	1.49	1.53	0.90	1.39
Phosphorus	0.72	0.97	0.91	trace	0.17	0.06	none	3.38	0.07
Ash.....	2.73	2.90	3.03	0.35	1.39	0.43	0.39	13.04	0.44
P <sub>2</sub> O <sub>5</sub> in ash	1.88	2.09	1.91	trace	0.47	trace	none	6.73	trace
	10	11	12	13	14	15	16	17	18
Carbon.....	51.21	46.67	51.87	....	51.95	51.65	....	52.02	49.59
Hydrogen..	6.85	6.19	6.89	....	6.86	6.66	....	7.00	6.68
Nitrogen...	16.18	15.89	16.65	16.31	16.08	16.02	16.09	16.45	16.34
Sulphur....	1.10	0.93	1.19	1.35	1.60	1.13	1.12	1.24	0.91
Phosphorus	0.46	2.53	trace	trace	trace	trace	trace	none	1.85
Ash.....	2.19	8.17	0.38	0.45	0.32	1.09	2.83	0.56	2.50
P <sub>2</sub> O <sub>5</sub> in ash	1.11	5.71	trace	trace	trace	trace	trace	none	1.79

Assuming that those of the foregoing preparations which contain phosphorus are compounds of protein with the nucleic acid,

which was separated from the aqueous extract of wheat germs and the composition of which is given on page 383 of this paper, and also assuming that all the phosphorus of these preparations is a part of the nucleic acid, we have calculated the composition of these preparations free from nucleic acid. The analyses were further calculated ash-free by subtracting the phosphorus pentoxide contained in the ash from the total ash, which seems permissible since the ash consisted almost wholly of metaphosphates of potassium and sodium, strongly indicating that the phosphorus pentoxide was derived from the nucleic acid. These calculations gave the following results:

TABLE II.—COMPOSITION OF LEUCOSIN CONTAINED IN THE PREPARATIONS FROM WATER EXTRACTS OF THE WHEAT EMBRYO.

	1	2	3	4	5	6	7	8	9
Carbon . . . .	52.93	52.75	52.41	52.57	52.57	52.47	52.93	53.23	52.64
Hydrogen..	7.12	7.16	7.38	6.85	6.91	7.08	7.13	7.09	7.02
Nitrogen...	16.45	16.68	16.94	16.26	16.27	16.55	16.06	16.30	16.46
Sulphur...	1.29	1.32	1.13	1.32	1.34	1.50	1.53	1.60	1.41
Oxygen....	22.21	22.09	22.14	23.00	22.91	22.40	22.35	21.78	22.47
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	10	11	12	13	14	15	16	17	18
Carbon . . . .	52.63	52.44	52.06	....	52.11	52.16	....	52.30	53.45
Hydrogen..	7.06	7.10	6.92	....	6.88	6.73	....	7.04	7.30
Nitrogen...	16.40	16.26	16.71	16.38	16.13	16.20	16.56	16.54	16.57
Sulphur....	1.17	1.34	1.19	1.35	1.60	1.14	1.15	1.24	1.16
Oxygen....	22.74	22.86	23.12	....	23.28	23.77	....	22.88	21.52
	100.00	100.00	100.00		100.00	100.00		100.00	100.00

Of these, preparation 1, 2, 3, 4, 13, 14, 15, 16, and 17 were obtained by coagulation with heat, 5 and 10 by coagulation with alcohol, 8 and 11 by saturation with sodium chloride, 6, 7, 9, and 12 by dialyzing salt solutions in water, and 18 by direct dialysis of the aqueous extract. Since some of these preparations formed the whole of the precipitable proteid contained in the extract, while others represented fractions, it is evident that all contain one and the same protein substance mostly combined with various proportions of nucleic acid.

Eliminating the nucleic acid, it thus appears that the composition of the protein part of those preparations which contain phosphorus is the same as that of the phosphorus-free proteid

preparations, although the former contain from very little up to more than 37 per cent. of nucleic acid.

Most of these preparations might, in accordance with custom, be called nucleoproteids, while 8 and 11 are, both in properties and composition, very much like nuclein. It is thus evident that these nucleoproteids and nucleins are nucleic acid compounds of protein which, owing to the high molecular weight of the nucleic acid, are more readily recognized as compounds than are those with acids of low molecular weight.

It is to be noted that these preparations show very diverse properties: some being like albumin; some like globulin; some being precipitated by saturation with salt, while others are not. As we have shown, these different properties are the result of changes caused by varying the conditions under which the proteid exists in the extract, and depend chiefly on the degree of acidity of the extract, whereby the numbers and kinds of acid molecules that combine with the protein molecule are altered.

Whatever may be the true cause of these changes, it is evident from the results here described, that the distinctions heretofore made between globulin and albumin, myosin and vitellin, etc., have very little value as a basis for classifying protein substances. This explains the difference between O'Brien's classification of leucosin as a myosin-like globulin, to which reference was made at the beginning of this paper, and our designation of it as an albumin, because of the ready solubility in water and coagulability by heat of the preparations which we had made.

Thus, preparation 18, weighing 9.17 grams, was insoluble in water and in salt solution and was not a precipitate of globulin, since in the filtrate from which it had separated on dialysis, only 0.87 gram of coagulable albumin was found instead of 9.5 grams as usually found by direct coagulation of the aqueous extracts; moreover the analysis shows it to be a compound of leucosin with 20 per cent. of nucleic acid.

On the preceding pages, it was shown that a small part of the precipitate, produced by saturating the aqueous extract with sodium chloride, is soluble in dilute salt solution and can be precipitated from this solution by dialysis, as a globulin-like substance, readily soluble again in salt solution. The precipitates thus obtained contain little or no nucleic acid, and have



very nearly the same elementary composition as leucosin, of which they are evidently compounds with a small proportion of some body of low molecular weight.

It is plain from these facts that O'Brien's myosin contains the same protein substance as my leucosin.

O'Brien's "*albumin*" coagulating at 75°–80° is unquestionably more of this same leucosin as shown by preparation 3, which formed about 25 per cent. of the total coagulable proteid. It has been the writer's experience that complete coagulation, especially in a solution quite free from salts, can be effected, if at all, only by heating the solution much above the lower coagulation temperature of the proteid to be separated.

From the whole seed we obtained leucosin with the same composition and general properties as from the embryo, but our preparations from the whole seed were free from phosphorus. This was probably because the proportion of nucleic acid to protein matter was smaller in the whole seed than in the embryo so that on extracting with water the nucleic acid did not form soluble compounds with the leucosin, but remained undissolved in combination with protein. In the following table is given the average of analyses of leucosin from the cereals.

TABLE III.—COMPOSITION OF LEUCOSIN PREPARED FROM VARIOUS CEREALS.

	Wheat embryo.	Wheat kernel.	Rye kernel.	Barley kernel.	Barley malt.	Maize <sup>1</sup> kernel.
Carbon .....	52.65	53.02	52.97	52.81	53.07	52.72
Hydrogen....	7.04	6.84	6.79	6.78	6.72	7.05
Nitrogen .....	16.43	16.80	16.66	16.62	16.71	16.82
Sulphur .....	1.32	1.28	1.35	1.47	} 23.50	1.32
Oxygen.....	22.56	22.06	22.23	22.32		22.05
	100.00	100.00	100.00	100.00	100.00	100.00

In an earlier paper on the "Chemical Nature of Diastase"<sup>2</sup> we pointed out that diastatic action appeared to be always associated with leucosin. Since our extracts of wheat embryo were so rich in leucosin, we determined the diastatic power of the

<sup>1</sup> This proteid was described by Chittenden and Osborne (*Am. Chem. J.*, 13, 327) as a myosin-like globulin, and was later (*This Journal*, 19, 525) designated maysin by the writer. Since we now find that leucosin may form compounds having the properties of globulin, it is probable that maysin and leucosin contain one and the same protein substance.

<sup>2</sup> *This Journal*, 18, 542; Report Conn. Agr. Exp. Sta., 1895, p. 239.



germ meal by extracting with four times its weight of water and found that, under the conditions of Lintner's test, 0.10 cc. of the extract so made, when added to 10 cc. of a 2 per cent. solution of soluble starch, formed within one hour, at 20°, enough sugar to reduce 5 cc. of Fehling's solution. The 0.10 cc. of extract corresponds to 25 milligrams of the germs, from which it is seen that this meal possesses high diastatic power, though it is inferior in this respect to active malt.

#### SODIUM CHLORIDE EXTRACT.

Wheat germ meal treated with 10 per cent. sodium chloride brine forms a dense jelly-like mass from which it is nearly impossible to separate the solution.

With 3 per cent. brine a manageable extract can be made by using from six to ten times as much solvent as meal. Thus, 100 grams of the meal treated with 600 cc. of 3 per cent. salt solution yielded in fifteen hours 400 cc. of clear filtrate. As has just been shown, the aqueous extract on dialysis, in consequence of a change which affects leucosin, deposits a large amount of proteid, chiefly in the coagulated form. In order to obtain preparations of the proteid substance soluble in salt solutions, but insoluble in water, which should be free from this coagulable albumin, we treated 2,000 grams of germ meal with 20 liters of 3 per cent. salt solution heated to 70°, whereby the leucosin was coagulated and the salt-soluble globulin brought into solution. The extract, neutral to litmus, was filtered clear, at once saturated with ammonium sulphate and the proteids thus precipitated collected on a filter, dissolved in water, and the clear solution dialyzed in running water.

Proteid matter separated on dialysis in spheroids which, like legumin, conglutin, and amandin, united to a plastic mass on the bottom of the dialyzer.

This precipitate was dissolved in brine, filtered absolutely clear, dialyzed for 48 hours, the large precipitate which separated allowed to settle, and the solution, which was nearly free from protein, decanted.

A portion of the precipitate was washed first with water, which rendered it opaque and dense, then with dilute and finally with absolute alcohol and dried over sulphuric acid. This weighed

5.22 grams, and is preparation 19. The rest of the precipitate was completely dissolved in 125 cc. of 10 per cent. salt solution. To this, water was added until its volume was 425 cc., thus making a salt solution of nearly 3 per cent. From this diluted solution a gummy deposit separated from which the liquid was soon completely decanted. The latter was further diluted with 325 cc. of water and the precipitate which resulted allowed to settle to a viscid transparent deposit. From this precipitate the solution was again decanted and dialyzed for 48 hours, but not more than a trace of globulin was deposited. The two precipitates produced by dilution were thoroughly washed with water and alcohol, dried over sulphuric acid and formed preparations 20 and 21, weighing respectively 11.4 grams and 8.15 grams. A part of each of these preparations was set aside for analysis and the rest, dissolved together in 10 per cent. salt solution, allowed to stand over night at 4°. The solution was then decanted from a slight sediment, filtered clear and heated to 80° in order to coagulate any leucosin which might be present, and after two hours filtered from a very small coagulum which had gradually formed.

This filtrate was dialyzed in water for four days and the globulin which separated was washed with water and with alcohol and dried over sulphuric acid, giving preparation 22.

The solution filtered from the first dialysis precipitates which yielded preparations 19, 20, and 21; was further dialyzed; a little globulin, which separated, was filtered out and the filtrate dialyzed into alcohol for four days. A precipitate was produced which, when washed with absolute alcohol and dried, weighed 25 grams. This substance consisted of proteid which will be described later, on page 402. Another series of fractional precipitations of this globulin-like proteid was made by extracting four kilograms of the oil-free germ meal with 27 liters 3 per cent. brine, heated to 67° at the time it was applied to the meal. The mixture was thoroughly stirred and thrown on filters. A clear filtrate of about 12 liters was finally obtained, which was saturated with ammonium sulphate. The precipitate produced was dissolved in water and its solution dialyzed for forty-eight hours, whereupon a large quantity of spheroids separated which on settling united to a coherent mass. This pre-

precipitate was washed by decantation with water, dissolved in brine, and its solution made faintly alkaline to litmus by cautiously adding N/10 potassium hydroxide solution. In order to separate phosphoric acid, a little calcium chloride solution was then added to this very slightly alkaline liquid and the latter, though apparently free from any precipitate of calcium phosphate, was filtered, whereby a little suspended matter was removed. The solution was made exactly neutral to litmus by adding 56 cc. N/10 hydrochloric acid and dialyzed for eighteen hours. A gummy precipitate, A, adhering to the bottom of the dialyzer, then separated, from which the solution, B, was decanted almost completely.

The precipitate, A, was dissolved in about 200 cc. of 5 per cent. brine and the liquid was poured into 800 cc. of water. The resulting flocculent precipitate settled rapidly to a coherent deposit from which the solution was decanted. The deposit was repeatedly washed by decantation with water, which caused it to lose its gummy character and become opaque, white, and granular. After dehydrating with absolute alcohol and drying over sulphuric acid it weighed 15.5 grams and was marked preparation 23. The solution marked B was further dialyzed for forty-eight hours when a second precipitate formed, which, like 23, completely dissolved in brine, to a solution perfectly neutral to litmus. This precipitate was washed by decantation with water, but the finer part settled so slowly that it was necessary to decant it together with the water. The sediment after exhausting with absolute alcohol and drying, weighed 23.5 grams, and formed preparation 24. On long standing, the decanted washings deposited the finely divided matter, which was then collected on a filter, dissolved in brine and its solution precipitated by water, giving 15.4 grams of preparation 25.

To determine the quantity of globulin contained in our oil-free germ meal, we treated 200 grams of the meal with 2,000 cc. of 3 per cent. salt solution heated to 65° and filtered the extract perfectly clear. Of this, 1,000 cc. were dialyzed until free from chlorides, when the precipitate of spheroids was filtered out, washed with water and with alcohol and dried over sulphuric acid. This preparation, 26, formed 5.05 per cent. of the oil-free meal.

To obtain a quantity of this globulin for digestion with pepsin, a quantity of germ meal was extracted with 3 per cent. salt solution heated to 70°, the extract was filtered clear and saturated with ammonium sulphate. The precipitate produced was dissolved in water and the resulting gummy and somewhat turbid solution filtered clear. The filtrate was dialyzed until the solution gave no turbidity on pouring into distilled water. The proteid, which had then separated in spheroids, was filtered out, washed by decantation with water and with alcohol and dried over sulphuric acid, giving 27.3 grams of preparation 27.

A part of the extract from which 27 had been prepared was mixed with an equal volume of N/10 potassium hydroxide, about twice the quantity necessary to neutralize the extract to phenolphthalein. The solution was then dialyzed in distilled water frequently renewed and in this way a considerable quantity of phosphorus was separated in the alkaline dialyzate. When all, or nearly all, which it was possible to separate in this way, had been removed, the solution in the dialyzer was neutralized with N/10 hydrochloric acid until it no longer reacted alkaline to litmus. This caused a turbidity. The acid was then further added until an acid reaction with litmus was obtained, producing a precipitate from which, after settling, the solution was decanted. The precipitate was then dissolved in brine, its solution filtered clear and dialyzed, whereby a substance was precipitated in spheroids, which was filtered out, washed with water and alcohol and formed preparation 28, weighing 3 grams.

These preparations had the following composition :

TABLE IV.—COMPOSITION OF PREPARATIONS EXTRACTED BY SODIUM CHLORIDE SOLUTIONS FROM THE WHEAT EMBRYO.

	19	20	21	22	23	24	25	26	27	28
Carbon .....	...	...	48.77	50.03	50.23	48.17	49.39	48.75	49.79	48.67
Hydrogen ..	...	...	6.44	7.04	6.89	6.54	6.78	6.52	6.76	6.56
Nitrogen ...	18.14	18.21	18.12	18.39	18.23	18.06	17.95	18.16	18.01	17.97
Sulphur....	0.49	0.56	0.51	0.60	0.53	0.55	0.48	0.63	0.61	0.61
Phosphorus	1.15	1.03	1.35	0.76	0.56	1.41	1.17	1.41	1.11	1.55
Ash .....	2.29	1.86	2.25	1.30	1.22	3.85	2.60	2.66	1.11	2.94
P <sub>2</sub> O <sub>5</sub> in ash.	1.66	1.34	1.68	0.84	0.80	2.00	1.82	2.00	0.68	2.30

These analyses, when calculated free from nucleic acid and ash, as was done for the albumin preparations, in the manner described on page 392, gave the following results :

TABLE V.—COMPOSITION OF THE GLOBULIN CONTAINED IN THE PREPARATIONS EXTRACTED FROM THE WHEAT EMBRYO BY SODIUM CHLORIDE SOLUTION.

	19	20	21	22	23
Carbon .....	....	....	51.37	51.58	51.40
Hydrogen .....	....	....	6.83	7.31	7.08
Nitrogen.....	18.59	18.59	18.62	18.70	18.45
Sulphur .....	0.57	0.63	0.60	0.66	0.57
Oxygen .....	....	....	22.58	21.75	22.50
			100.00	100.00	100.00
	24	25	26	27	28
Carbon .....	51.56	51.86	51.40	51.98	51.70
Hydrogen .....	7.07	7.19	6.94	7.12	7.05
Nitrogen.....	18.85	18.41	18.71	18.37	18.53
Sulphur .....	0.67	0.55	0.75	0.70	0.75
Oxygen.....	21.85	21.99	22.20	21.83	21.97
	100.00	100.00	100.00	100.00	100.00

These figures plainly show that our globulin preparations are mixtures of nucleates of one and the same protein substance and contain from 5 to 15 per cent. of nucleic acid. The preparations contain the same protein as the globulin which one of us has previously described as occurring in the kernel of wheat, rye, barley, and maize. In the entire kernel, so little of this globulin is present that it is difficult to prepare it pure therefrom. For this reason, we think, the analyses given below do not agree as closely as they might otherwise be expected to. From the whole seed this globulin is obtained entirely free from phosphorus, which we attribute to the much greater proportion of proteid matter to nucleic acid, in the seed, compared with that existing in the wheat embryo.

TABLE VI.—COMPOSITION OF THE GLOBULIN CONTAINED IN VARIOUS CEREALS.

	Wheat embryo.	Wheat <sup>1</sup> kernel.	Rye <sup>2</sup> kernel.	Maize <sup>3</sup> kernel.	Barley <sup>4</sup> kernel.
Carbon .....	51.57	51.03	51.19	51.99	50.88
Hydrogen .....	7.07	6.85	6.74	6.81	6.65
Nitrogen .....	18.60	18.39	18.19	18.02	18.10
Sulphur .....	0.65	0.65	23.88	0.66	24.37
Oxygen.....	22.11	23.08		22.52	
	100.00	100.00	100.00	100.00	100.00

<sup>1</sup> *Am. Chem. J.*, 15, 392.<sup>2</sup> This Journal, 17, 429; also Report of Conn. Expt. Station for 1894, p. 147.<sup>3</sup> *Am. Chem. J.*, 13, 327, 385 and 15, 20.<sup>4</sup> This Journal, 17, 539; also Report of Conn. Expt. Station for 1894, p. 165.

Having determined the composition of this globulin-like proteid and also that of the albumin, it became clear that several preparations obtained from the aqueous extract were mixtures of these two substances, thus showing the globulin to be present to some extent in the aqueous extract.

As noted on page 388, when 2,000 cc. of an aqueous extract of about 650 grams of the meal were dialyzed in running water for four days, a dense turbidity was formed which could not be removed by filtration. This, however, on adding a little hydrochloric acid, was converted into a precipitate, which was readily dissolved by adding sodium chloride sufficient to make a 3 per cent. solution, and was precipitated from this solution by dialysis. We thus obtained 9 grams of preparation 29, which, dried at  $110^{\circ}$ , had the following composition:

## COMPOSITION OF PREPARATION 29.

	I.	II.	Av.	Corrected for ash and nucleic acid.	Calculated for 60 per cent. globulin, 40 per cent. leuco- sin.
Carbon .....	48.30	47.92	48.11	51.70	51.95
Hydrogen .....	6.49	6.41	6.45	7.07	7.07
Nitrogen .....	17.40	17.24	17.32	17.74	17.74
Sulphur .....	0.83	0.85	0.84	1.08	0.91
Phosphorus .....	1.91	....	1.91	....	....
Oxygen .....	....	....	....	22.51	22.53
Ash .....	3.95				
P <sub>2</sub> O <sub>5</sub> in ash .....	2.95			100.00	100.00

This analysis corresponds pretty nearly with that of a mixture of 60 per cent. of the globulin with 40 per cent. of leucosin, except that the amount of sulphur found was somewhat greater than that calculated.

After heating another portion of the same aqueous extract to  $65^{\circ}$  for some time and filtering off the coagulum, the filtrate was dialyzed for five days into alcohol and the precipitate thereby produced filtered out and exhausted with water. The residue of proteid matter coagulated by alcohol, weighing 6.7 grams and marked preparation 30, was then dried at  $110^{\circ}$  and analyzed with the following results:

## COMPOSITION OF PREPARATION 30.

		Corrected for ash and nucleic acid.	Calculated for globulin 40 per cent., leucosin 60 per cent.
Carbon.....	49.49	51.80	52.13
Hydrogen .....	6.81	7.14	7.03
Nitrogen.....	16.87	17.32	17.30
Sulphur .....	0.93	1.14	1.05
Phosphorus .....	0.89	....	....
Oxygen .....	....	22.60	22.49
Ash.....	4.00	—	—
P <sub>2</sub> O <sub>5</sub> in ash.....	2.01	100.00	100.00

This analysis corresponds quite nearly with that of a mixture of 40 per cent. of the globulin with 60 per cent. of the albumin.

## THE PROTEOSE OF THE WHEAT EMBRYO.

In making the preparations already described considerable quantities of crude proteose were obtained from both the aqueous and sodium chloride extracts. After the leucosin and the globulin had been separated as completely as possible, the solutions containing the proteoses, as well as the unseparated residues of other proteids, were dialyzed into alcohol and the precipitates produced washed and dried over sulphuric acid.

A mixture, weighing 15.4 grams, was made by uniting several such preparations that had been obtained from aqueous extracts from which most of the other proteids had been separated, without heat, by saturating with sodium chloride and dialysis into alcohol. The mixture contained much matter made insoluble in water by the final treatment with alcohol. This was filtered out, washed thoroughly with water and with alcohol and when dried weighed 4.18 grams, and was marked preparation 31. The filtrate from this was saturated with ammonium sulphate, the precipitate redissolved and again precipitated in the same way. The solution of the second precipitate was dialyzed in cold distilled water until free from sulphate, and then for several days in alcohol. The precipitate thus produced was dissolved in water, a little insoluble matter filtered out, and its clear solution saturated with sodium chloride, which produced a small precipitate. This was filtered out, dissolved, and its solution dialyzed in water. The salt-saturated filtrate was likewise dialyzed and when both solutions were free from chlorine the dialyzers were

transferred to alcohol and the proteose thereby precipitated. The proteose separating on saturation with salt, gave 0.6 gram of preparation 32; that from the salt-saturated solution, 0.97 gram of preparation 33. This small yield of proteose indicates great impurity of the original crude product and shows that the proportion of proteose to other proteids is very small.

Another crude product was obtained by dialyzing into alcohol an aqueous extract, after separating leucosin which had been coagulated by heat. This, weighing 35 grams, was dissolved in water and the insoluble matter filtered out, washed and dried, giving preparation 34, weighing 7.26 grams.

The filtered solution was saturated with ammonium sulphate, the precipitate dissolved in water, and the clear solution dialyzed in distilled water until free from sulphates, and then in alcohol. The substance thus separated was again dissolved in water, and its solution saturated with salt; the precipitate thus produced was dissolved in water and its solution, as well as the salt-saturated filtrate, were dialyzed in water. When free from chlorine, these solutions were dialyzed in alcohol and yielded, respectively, preparations 35, weighing 4 grams and 36, weighing 1.84 grams.

Another preparation of crude proteose was obtained by extracting the meal with 3 per cent. sodium chloride solution heated to 70°, dialyzing the extract in water, coagulating the leucosin by heat and precipitating the proteose by dialysis in alcohol. A mixture of such preparations, weighing 31.6 grams, was treated with water, the insoluble matter filtered out, washed and dried, giving 5.16 grams of preparation 37.

The filtered solution was saturated with ammonium sulphate, the precipitate dissolved in water, the solution dialyzed in distilled water till free from sulphate, and then in alcohol. The separated proteose was redissolved in water and its solution saturated with sodium chloride. The precipitate which resulted was filtered out, dissolved in water and its solution, as well as the salt-saturated filtrate, was dialyzed in water till free from chlorine, and finally in alcohol.

The products thus obtained, formed, respectively, preparations 38, weighing 0.75 gram and 39, weighing 1.35 grams. One other proteose preparation was made from the aqueous



extract previously described on page 390 from which the phosphorus was largely separated by making it slightly alkaline and adding calcium chloride. After heating the extract to boiling and filtering out the coagulum, the filtrate was dialyzed into alcohol, the resulting precipitate dehydrated with absolute alcohol, dried over sulphuric acid, redissolved in water, and precipitated by saturating with ammonium sulphate. The gummy precipitate, having the general appearance and properties of similar precipitates of the proteoses obtained by the action of pepsin, was dissolved in water, dialyzed free from sulphates, and then precipitated by dialysis in alcohol, giving 2 grams of preparation 40.

These preparations were dried at  $110^{\circ}$  and analyzed with the following results :

TABLE VII.—COMPOSITION OF ALCOHOL-COAGULA AND OF PROTEOSE PREPARED FROM THE WHEAT EMBRYO.

	Residues of other proteids coagulated by alcohol.			Proteose precipitated by sodium chloride.			Proteose soluble in saturated NaCl sol.			
	31	34	37	32	35	38	33	36	39	40
Carbon . . .	52.36	49.44	51.93	....	49.94	....	48.46	48.70	48.44	48.99
Hydrogen .	6.98	6.85	6.87	....	6.80	....	6.70	6.73	6.71	6.85
Nitrogen ..	16.01	16.00	16.30	16.79	17.08	16.26	16.91	16.76	16.16	16.89
Sulphur ..	1.85	4.08	1.30	....	1.24	....	27.93	27.81	28.69	1.10
Oxygen ..	22.80	23.63	23.60	....	24.94	....				26.17
	100.00	100.00	100.00		100.00		100.00	100.00	100.00	100.00
Ash .....	0.81	14.13	0.95		0.30	0.77	1.13	1.00	0.74	1.27

From these analyses it is seen that the matter insoluble in water, forming preparations 31, 34, and 37 consists of coagulated proteid apparently mostly derived from leucosin. The high proportion of sulphur in 31 and 34 is due to calcium sulphate, precipitated by alcohol from the aqueous extract.

The remaining preparations have the low percentage of carbon, characteristic of proteoses made by pepsin digestion.

Whether the proteose precipitated by saturating its solution with salt is a different protein substance from that soluble in saturated salt solution or whether difference in solubility is due to the presence of different acid compounds of one and the same protein substance, is not demonstrated, but the agreement shown by these analyses, considering the difficulty of making quite pure preparations, indicates that the latter is the case.

**The Proportions of the Various Proteid Substances of the Wheat Embryo.**

Twenty grams of fresh germ meal, from which the ether-soluble constituents had *not* been separated, were treated with 500 cc. of water and after shaking for some time, the extract was filtered clear. Two portions, of 100 cc. each, were treated with a few drops of very dilute hydrochloric acid and heated in a boiling water-bath. The coagulum which separated was collected on a filter and its nitrogen determined. To the filtrate from one coagulum, tannin was added and nitrogen was determined both in the precipitate and in the filtrate. Another lot of 20 grams was treated in the same way and nitrogen determined in the heat-coagulum formed in each of two portions of 100 cc. The amount of nitrogen corresponding to one gram of germ meal was found in the four coagula to be, 0.0163 gram, 0.0156 gram, 0.0159 gram, and 0.0162 gram; in the tannin precipitate 0.0062 gram; and in the solution filtered from the latter 0.0062 gram.

Twenty grams of germ meal were extracted with 500 cc. of 3 per cent. sodium chloride solution heated to 70°, whereby the leucosin was coagulated and the globulin and proteose dissolved. Of the clear filtered extract, 100 cc. yielded with tannin a precipitate containing 0.0166 gram nitrogen per gram of meal extracted.

Two portions of the meal, each of one gram, were exhausted with 3 per cent. sodium chloride solution heated to 70°, and nitrogen determined in the residues. The 0.0331 and 0.0309 gram of nitrogen found in the residues were from the leucosin and insoluble nitrogenous bodies, so that the nitrogen belonging to the latter equaled 0.0171 gram and 0.0149 gram. From the average of these figures we find the following amounts of the different forms of nitrogen in one gram of the wheat germ meal.

	Nitrogen. Gram.
Insoluble in water and salt solution .....	0.0160
Insoluble in water but soluble in salt solution	0.0100 = globulin nitrogen.
Soluble in water and coagulable by heat ....	0.0160 = albumin      “
Soluble in water, uncoagulable by heat, precipitable by tannin .....	0.0050 = proteose      “
Not precipitable by tannin .....	0.0060 = non-proteid      “
Total .....	0.0530
Found by direct nitrogen determination ....	0.0531

We have shown that the coagulated leucosin preparations contain about 10 per cent. of nucleic acid, the globulin about 15 per cent., while those of the proteose contain none. Deducting these quantities from the nitrogen given in the table, we find 9.5 per cent. of the embryo to be leucosin, 4.84 per cent. to be globulin, and 3.03 per cent. to be proteose.

The bodies which are represented by the insoluble nitrogen, we have been unable to separate from the embryo. The residue after extraction with hot salt solution contained 0.0076 gram of phosphorus. Since there was in this residue about 0.1000 gram of coagulated leucosin, in which we have usually found about 1 per cent. of phosphorus, we have 0.0061 gram of phosphorus remaining over. In view of the large proportion of nucleic acid found in the extracts of the embryo, it is not improbable that this phosphorus mostly belongs to nucleic acid, in which case there would be about 6.75 per cent. of nucleic acid containing 0.0108 gram of nitrogen, which leaves only 0.0052 gram of nitrogen for proteid matter in the insoluble residue. It seems probable, therefore, that this insoluble nitrogen largely belongs to compounds of the proteid with relatively much nucleic acid.

#### DIGESTION OF THE PHOSPHORUS-CONTAINING PROTEIDS WITH PEPSIN-HYDROCHLORIC ACID.

*Leucosin Nucleate.*—Ten grams of the coagulated albumin, preparation 2, were suspended in 400 cc. of water and dissolved by adding 100 cc. of N/10 potassium hydroxide solution. To the nearly clear solution which resulted, an equal volume of 0.4 per cent. hydrochloric acid was added, together with some pepsin, and the mixture digested at 37°. In a short time the solution became perfectly clear, but later deposited a large coherent precipitate, which gradually contracted, but at the same time retained the form of the lower part of the beaker. From this the clear solution was decanted, the precipitate thoroughly washed by decantation, suspended in water and dissolved by adding 28 cc. of N/10 potassium hydroxide solution, an amount of alkali just sufficient to dissolve all the substance and at the same time make the solution neutral to litmus. When to this solution decinormal acid was gradually added, no precipitate appeared until nearly one-half the quantity of acid required for

complete neutralization had been added, but with 28 cc., the solution was neutralized and also completely precipitated, the addition of 2 cc. more acid giving no turbidity in the solution filtered from the precipitate. This precipitate was washed with water and with alcohol and dried over sulphuric acid, forming preparation 41, weighing 1.54 grams.

To precipitate this substance a quantity of acid was added exceeding that of the alkali employed for solution by just 2 cc. The filtrate from the precipitate, however, required not 2 cc. of alkali, but 8.5 cc. for neutralization to phenolphthalein, showing 6.5 cc. of alkali to have been neutralized by the acid of the nuclein originally dissolved. The neutralized filtrate left, on evaporation, 0.3975 gram of substance, the aqueous solution of which was precipitated by hydrochloric or nitric acid, but *not* by ammonium molybdate solution until after boiling with acid for some little time, when yellow phosphomolybdate was precipitated. These facts indicate the presence in this filtrate of a nucleic acid.

More nuclein was made from the same preparation, 2, by suspending 30 grams in 0.2 per cent. hydrochloric acid, containing pepsin, which, even at 20°, caused within two hours complete solution of the coagulated proteid. The solution was digested at 37° for forty-eight hours, during which time much nuclein separated, having the appearance and properties of the preparation just described.

After decanting the clear solution and thoroughly washing the residual nuclein, the latter was suspended in water and dissolved in 72 cc. N/10 potassium hydroxide. The solution thus obtained was made neutral to litmus by adding 11 cc. of N/10 hydrochloric acid, but no precipitate appeared till 1.5 cc. more of acid were added. To the solution 72 cc. N/10 hydrochloric acid were added, giving a precipitate which, when washed and dried, made preparation 42 and weighed 3.4 grams. The filtrate from this precipitate, as in the former case, was strongly acid, requiring 12 cc. of N/10 potassium hydroxide to neutralize it to phenolphthalein. Two other preparations of nuclein were made from 8.493 grams of 8, and 9.804 grams of 11, both being substances precipitated from the aqueous extract by saturating with sodium chloride. Each portion was suspended in about 300 cc. of 0.2 per cent. hydrochloric acid, containing 0.1 gram of pepsin and,

with frequent stirring, digested at 40° for twenty-four hours. Throughout the digestion a large part of the substance remained undissolved. An equal volume of 0.2 per cent. hydrochloric acid, containing 0.1 gram of pepsin, was again added to each and the digestion continued for twenty-four hours longer. The insoluble matter which remained was not coherent like the two former nuclein products, but consisted of a white, very finely divided substance which was easily filtered out and washed. After dehydrating with absolute alcohol these preparations were dried over sulphuric acid; from 8, 4.04 grams of preparation 43 were obtained and from 11, 4.16 grams of 44.

*Globulin Nucleate.*—Fifteen grams of a mixture of nearly equal parts of the globulin preparations 23 and 24 were next suspended in 0.2 per cent. hydrochloric acid, containing 0.2 gram of pepsin, which, within a short time, almost completely dissolved the proteid matter. From this solution, on further digestion, the nuclein separated, forming a coherent deposit. After seventy-two hours' digestion, the clear solution was decanted, the deposit dissolved in a little ammonia and its solution filtered perfectly clear from a very slight gelatinous residue. The resulting solution was then treated with acetic acid, added in excess of the amount necessary to neutralize the solution to litmus. Since, even on standing, the precipitate so produced separated imperfectly, an equal volume of alcohol was added. The substance, which then separated well, was filtered out, washed with dilute and with absolute alcohol and dried over sulphuric acid, giving 2.38 grams of preparation 45, or about 16 per cent. of the original substance.

The filtrate from the acetic acid precipitate gave a further slight precipitate on adding hydrochloric acid, which had properties characteristic of nucleic acid.

Still another preparation of nuclein was made from the globulin by suspending 10 grams of 27 in water and adding 50 cc. of N/10 potassium hydroxide. This solution was neutralized and an equal volume of 0.4 per cent. hydrochloric acid at once added, producing a turbid solution, which, however, contained no visible particles. To this, pepsin was added and the mixture digested for forty hours, during which time a coherent deposit of nuclein formed on the bottom of the beaker. From this,

the clear solution was decanted. The deposit was then thoroughly washed with water and dissolved in 43 cc. of N/10 potassium hydroxide. To this clear solution 43 cc. of N/10 hydrochloric acid were added, causing a gummy precipitate which could not be filtered until 15 cc. more acid had been added, when the precipitate rapidly settled as a coherent deposit, from which the solution was soon decanted. This solution required for neutralization to litmus 16 cc. N/10 potassium hydroxide, and to phenolphthalein 18 cc. The precipitate, when washed and dried, gave 2.2 grams of preparation 46.

These six preparations were all dried at 110° and analyzed with the following results:

TABLE VIII.—COMPOSITION OF NUCLEIN FROM THE PROTEIDS OF THE WHEAT EMBRYO.

	41	42	43	44	45	46
Carbon.....	44.87	44.35	42.68	43.35	39.42	41.92
Hydrogen.....	5.82	5.77	5.45	5.47	5.03	5.25
Nitrogen.....	16.04	16.64	16.12	16.01	16.05	17.00
Sulphur .....	0.97	1.03	0.65	0.85	0.53	0.46
Phosphorus...	4.58	5.07	5.32	4.88	5.27	5.63
Ash.....	0.60	0.78	1.72	1.72	17.42	1.17
P <sub>2</sub> O <sub>5</sub> in ash....	0.29	0.55	1.24	0.94	10.56	0.69

If we subtract from the total ash the amount of phosphorus pentoxide found in it, we shall have a determination of the bases contained in the ash of these preparations.

We have calculated these analyses of nuclein free from the bases of the ash and from nucleic acid, in the way previously described, with the following results:

TABLE IX.—COMPOSITION OF PROTEIN MATTER CONTAINED IN THE NUCLEIN.

	41	42	43	44	45	46
Carbon .....	53.65	54.77	51.80	52.36	52.30	51.64
Hydrogen .....	7.23	7.46	6.85	6.73	6.91	6.60
Nitrogen .....	16.68	17.56	16.31	16.31	19.31	18.83
Sulphur .....	1.98	2.37	1.61	1.89	1.53	1.25
Oxygen.....	20.46	17.84	23.43	22.71	19.95	21.58
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The composition of the proteid matter in 43 and 44 is very nearly that of leucosin except as regards sulphur, the amount of

which is decidedly greater. On the other hand, 41 and 42, which also were derived from preparations whose protein matter was leucosin, differ in composition very decidedly from that substance. This is probably because on pepsin digestion the substance of preparations 43 and 44 remained throughout undissolved, whereas 41 and 42 separated on pepsin digestion from nearly clear solutions and therefore doubtless their protein matter had been to some degree altered by the pepsin before separating as an insoluble compound with nucleic acid. The two nucleins, 45 and 46, from the globulin which also had separated from solution, show similar differences in composition when compared with the unaltered globulin, carbon and nitrogen being higher and sulphur very much higher than in the globulin. The greatly increased proportion of sulphur would indicate that sulphur in some acid form had split from the proteid molecules undergoing hydrolysis and had become a part of the insoluble nuclein, as did the nucleic acid.

## CONCLUSION.

The embryo of the wheat kernel contains:

1. A *nucleic acid* in considerable quantity. This acid is insoluble in water, forms soluble as well as insoluble compounds with proteid substances, and on hydrolysis yields guanin, adenin, phosphoric acid, and other products not yet identified. It has the following composition:

## NUCLEIC ACID.

Carbon .....	36.48
Hydrogen .....	4.48
Nitrogen .....	16.17
Phosphorus .....	8.96
Oxygen .....	33.91
	<hr/>
	100.00

This acid is not identical with any nucleic acid heretofore described. On hydrolysis it does not yield any form of sugar. From guanylic acid recently described by Bang it also differs distinctly, in that its potash salt is extremely soluble in cold water and the ratio of phosphorus to nitrogen, being 1 to 4 instead of 1 to 5.

2. *Leucosin*, an albumin (yield about 10 per cent. of the

embryo) formerly found by the writer in small quantity in the whole kernel of wheat, rye, and barley, and abundantly in malt. Leucosin begins to separate as a flocculent coagulum when the very slightly acid aqueous extract of the wheat kernel or wheat embryo is heated to  $52^{\circ}$ . Even after long heating at  $65^{\circ}$ , the leucosin is only partly separated, and about one-third more coagulum of the same elementary composition is obtained on raising the temperature from  $65^{\circ}$  to  $100^{\circ}$ .

By saturating extracts of the kernel or of the embryo with sodium chloride, the leucosin is largely precipitated from the former as a substance readily soluble again in water, from the latter as an insoluble compound containing about 30 per cent. of nucleic acid. From the latter precipitate, dilute salt solution extracts a small amount of nearly phosphorus-free proteid, which behaves like a globulin, being precipitated by dilution or by dialysis, but having essentially the same ultimate composition as leucosin.

By dialyzing the aqueous extract in water, nearly all the leucosin contained in it is precipitated, not like a globulin, but as an insoluble compound containing about 20 per cent. of nucleic acid. The following figures give the average of accordant analyses, calculated nucleic acid-free, of 18 different preparations representing complete as well as fractional precipitations under the above and other conditions. These figures agree closely with the composition of the leucosin of wheat, rye, barley, and malt.

LEUCOSIN.	
Carbon .....	52.65
Hydrogen .....	7.04
Nitrogen .....	16.43
Sulphur.....	1.32
Oxygen .....	22.56
	<hr/>
	100.00

3. A *globulin*, precipitated in spheroids by dialysis and by dilution as a coherent deposit. The yield is about 5 per cent. of the embryo. The solution of this globulin in 10 per cent. sodium chloride brine becomes turbid on heating to about  $87^{\circ}$ , and at  $90^{\circ}$ , on continued heating, a considerable flocculent coagulum separates.



Our preparations of this globulin contained from 6 to 17 per cent. of nucleic acid, most of them from 12 to 15 per cent. From this the proteid could not be separated by fractional precipitation.

Analyses of ten different preparations of this globulin gave very closely agreeing figures when calculated free from nucleic acid, the average of which is as follows :

## GLOBULIN.

Carbon .....	51.57
Hydrogen .....	7.07
Nitrogen .....	18.60
Sulphur .....	0.65
Oxygen .....	22.11
	<hr/>
	100.00

In composition and properties this globulin agrees with that found by the writer in the kernels of wheat, rye, and barley. So far as we have been able to observe, it differs from edestin, the crystalline globulin obtained from seeds of hemp, flax, and squash only in containing two-thirds as much sulphur.

4. *Proteose*, precipitated by saturating the aqueous extract, freed from globulin and albumin, with salt. One preparation, 35, was phosphorus-free, and had the following composition :

## PROTEOSE.

Carbon .....	49.94
Hydrogen .....	6.80
Nitrogen .....	17.08
Sulphur .....	1.24
Oxygen .....	24.94
	<hr/>
	100.00

5. *Proteose*, soluble in the salt-saturated solution filtered from the foregoing proteose and obtained free from phosphorus by precipitating with alcohol its solution freed from salt by dialysis. The average of analyses of four preparations of this proteose is the following :

## PROTEOSE.

Carbon .....	48.65
Hydrogen .....	6.75
Nitrogen .....	16.68
Sulphur .....	1.10
Oxygen .....	26.82
	<hr/>
	100.00

These proteoses together form about 3 per cent. of the embryo.

6. About one-third of the total nitrogen of the embryo is not extracted by water and salt solutions and appears to belong to insoluble compounds. This nitrogen is accompanied by phosphorus corresponding to about 6.75 per cent. of nucleic acid, which would contain two-thirds of this insoluble nitrogen. It seems probable, therefore, that this insoluble nitrogen belongs largely to insoluble compounds of nucleic acid and protein.

7. These phosphorus-containing preparations of globulin and leucosin, when digested with pepsin-hydrochloric acid, yield nuclein in proportion to the phosphorus which they contain. Calculated free from nucleic acid, the analyses of these nucleins show the protein constituent to have nearly the same composition as the proteid from which they were derived, the most marked difference being a greater proportion of sulphur in the former.

8. The proteids of the embryo differ from those of the dormant endosperm, of this as well as of other seeds, in the facility with which they undergo changes. These changes are the result of a redistribution of acids among the protein and other basic molecules, so that compounds form in the extracts of the embryo which contain various proportions of nucleic acid according to the changing conditions.

The writer has shown that the globulin, edestin, forms crystalline compounds with one and with two molecules of acid and also compounds with a greater number of acid molecules. There is reason to believe that all other native protein substances form similar compounds; in other words, that proteins are distinctly polyacid bases and that the acid characters which proteids display are due to acids united to their protein molecules probably in the same manner as in the salts of the purin bases.

These nucleic acid compounds of the protein constituents of the wheat embryo appear to be compounds of this order. According to this view, no special distinction can be made between nucleins and nucleoproteids, the former being simply compounds containing a greater number of molecules of nucleic acid united to one molecule of protein.

That the wheat embryo in fact contained the same nucleic acid *compounds* as we have obtained from the extracts, is highly

improbable. All that we can conclude is that the embryo contains the different protein substances described, together with nucleic acid, and that these may unite to form a number of different compounds according to the conditions which prevail at any given time.

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## THE PROTEIDS OF THE EGG YOLK.<sup>1</sup>

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The yolks of a large number of freshly laid hens' eggs were broken up by straining through a sieve and mixed with an equal volume of saturated pure sodium chloride brine. A somewhat turbid solution resulted, which was shaken out with about one-third its volume of ether, containing a little alcohol. After standing one night, a clear reddish ethereal layer separated, leaving the pale yellow aqueous solution almost clear. After shaking out a second time with ether the aqueous solution was dialyzed for forty-eight hours, whereupon a large quantity of proteid separated in spheroids which united to a salvy mass. This was freed, as far as possible, from the liquid, by draining on filters, redissolved in 10 per cent. brine and its solution dialyzed for three days. From the semisolid mass thus obtained the liquid was decanted and the precipitate dissolved in 10 per cent brine. A little transparent gummy substance (lecithin?) remained undissolved which rendered filtration very difficult. By filtering under considerable pressure on a thick layer of paper pulp about 700 cc. of *perfectly clear* filtrate, *a*, and 2,000 cc. of very nearly clear filtrate, *b*, were obtained. The latter, *b*, was dialyzed for four days, when the large deposit was filtered out and treated with about a liter of salt solution. A gelatinous, almost pasty mixture resulted, which was shaken out with ether. The two liquids at once separated, the ethereal being clear and strongly yellow in color and the aqueous almost perfectly clear and not at all gummy. Shaken out three times more with ether, this aqueous solution became suddenly opaque and gelatinous. The mass was dialyzed free from chlorides, the solid deposit was washed with alcohol and with ether and dried over sulphuric

<sup>1</sup> From advance sheets of the report of the Connecticut Agricultural Experiment Station for 1899, communicated by the authors.

acid, giving preparation 1, weighing 60 grams. The *clear* solution, *a* (700 cc.), was diluted with three volumes of distilled water, and allowed to stand over night at a temperature of 6°. The proteid, which had separated on dilution, soon settled as a clear, transparent layer, from which the clear solution, *c*, was decanted completely. The proteid was readily and completely soluble in 10 per cent. brine to a perfectly clear pale yellow solution, which, when dialyzed until wholly free from chlorides, yielded the proteid in spheroids that subsequently united to a semisolid mass. The latter was filtered out, washed thoroughly with water and with alcohol, and dried over sulphuric acid, giving 32.1 grams of preparation 2. The solution, *c* (decanted from the precipitate produced by dilution that yielded 2), was treated with 1,000 cc. more water. This caused a precipitate which within two hours formed a semifluid deposit. From this the solution, *d*, was decanted, and the deposit dissolved in brine yielding a perfectly clear solution, which was dialyzed until free from chlorides.

The proteid thus precipitated was filtered out, washed with absolute alcohol as long as anything could be removed thereby, and then dried over sulphuric acid, giving preparation 3, weighing 16.5 grams.

The solution, *d*, was dialyzed free from chlorides, the precipitated spheroids were filtered out, washed with absolute alcohol and dried over sulphuric acid, making 5 grams of preparation 4.

The solution, page 413, filtered after forty-eight hours' dialysis from the substance that yielded the foregoing preparations, was further dialyzed until almost all its dissolved proteid had separated.

The precipitate thus produced was filtered out, dissolved in brine and the solution shaken out three times with ether. On shaking out the third time, the solution suddenly changed to an opaque jelly. This was then placed in a dialyzer, and when all the salt had been removed, the insoluble proteid was washed with absolute alcohol until everything soluble therein was extracted. Dried over sulphuric acid, this preparation, 5, weighed 75 grams. All these preparations were dried at 110° and analyzed with the following result:

	1	2	3	4	5
Carbon .....	50.82	51.21	51.10	50.69	50.48
Hydrogen .....	7.11	7.07	7.21	7.06	7.11
Nitrogen .....	16.04	16.11	16.23	16.40	15.50
Sulphur .....	1.11	1.05	1.00	1.05	1.02
Phosphorus.....	0.91	0.81	0.79	1.20	0.96
Ash.....	2.37	2.49	1.56	3.23	3.19
P <sub>2</sub> O <sub>5</sub> in ash.....	1.65	1.79	1.14	2.30	2.15

The ash of all these preparations consisted of sodium metaphosphate containing about 70 per cent. of P<sub>2</sub>O<sub>5</sub>. We have therefore subtracted from the total ash its phosphorus pentoxide, the remainder representing the ash to be deducted in calculating the percentage composition of the proteid substance.

Any chlorine or sulphur that might belong to the ash would necessarily be lost during incineration.

Calculating these preparations free from ash, as thus corrected, we have :

	1	2	3	4	5
Carbon .....	51.18	51.56	51.31	51.16	51.00
Hydrogen .....	7.14	7.12	7.24	7.12	7.18
Nitrogen.....	16.16	16.23	16.30	16.55	15.66
Sulphur .....	1.12	1.06	1.00	1.06	1.03
Phosphorus.....	0.92	0.82	0.79	1.21	0.97
Oxygen.....	23.48	23.21	23.36	22.90	24.16
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

1 and 5 represent the two main fractions that weighed 60 and 75 grams respectively ; while 2, 3, and 4 represent fractions of 1, whose weights were respectively 32, 16.5, and 5 grams.

In composition all are nearly alike. A little more phosphorus was found in 4 than in the other preparations, probably because a larger proportion of some phosphorus-containing acid was combined with the protein of this final, very soluble fraction, which formed less than 10 per cent. of the total vitellin.

We have not yet succeeded in preparing this phosphorized acid free from proteid. The body, which we have thus prepared from egg yolk and analyzed, is not present, as such, in the egg, for the proteid substances of the yolk are readily and wholly soluble in salt solution, whereas all these preparations are entirely insoluble in salt solution. Insolubility in the cases of 2, 3, and 4 was caused by washing with alcohol, which at the

same time removed much lecithin. Lecithin was not present as an admixture, but was chemically combined with the proteid, forming a compound soluble in saline solutions and having the properties of globulin, as is shown by the following experiments.

A. The alcoholic washings from the three successive fractions, 2, 3, and 4, were evaporated and left residues of crude lecithin weighing 6.4796, 3.5913, and 1.3150 grams, respectively. Adding these quantities to the weights of the corresponding fractions dried at  $110^{\circ}$ , we have the amounts of lecithin-protein compound originally composing them. These contained 18.00, 19.4, and 22.23 per cent. of lecithin, respectively.

B. The yolks of two eggs were directly extracted with ether until practically nothing more was removed. The residual matter was then, as far as possible, dissolved in 10 per cent. salt solution, filtered perfectly clear and the solution diluted with water until an abundant precipitate separated. This was filtered out, dissolved in salt solution, and filtered perfectly clear. This solution and that filtered from the precipitate previously produced by diluting with water were separately dialyzed.

The proteid precipitates thus obtained were filtered out and washed with water and alcohol. The part precipitated by dilution was found to contain 17.5 per cent. of lecithin, that which remained in the diluted brine, 22.3 per cent.,—results in pretty close accord with those already stated.

C. Part of a large quantity of yolk vitellin which had suddenly become insoluble on shaking with ether, was thoroughly washed with water and then completely extracted with alcohol until all the lecithin, equal to 13.31 per cent. was removed. The solution, from which the above large quantity of insoluble proteid had originally separated, still contained a little protein matter and was therefore saturated with ammonium sulphate and the salt solution of the precipitate so produced was dialyzed. The substance which then separated in spheroids, after thorough washing with water, was still readily soluble in salt solution, but when washed with alcohol became insoluble and yielded to the alcohol 24.2 per cent. of lecithin.

Hoppe-Seyler considered this lecithin to be chemically combined with the proteid, with which view our experience is in full harmony. It is not possible that such large quantities of

lecithin are simply admixed with the protein matter, for were this the case it could be readily removed by ether. Furthermore we could not dissolve a mixture of globulin and lecithin in brine and obtain a clear solution easy to filter. That the proteid should unite with lecithin is to be expected, since protein readily combines with acids. We must, accordingly, consider the protein of egg yolk to be largely, if not wholly, a lecithin compound which dissolves in salt solution, and behaves like a globulin.

Saline extracts of egg yolk, like those of plant-seeds, contain, according to circumstances, mixtures of compounds of the protein molecule with several different numbers of molecules of lecithin, of which the more soluble compounds contain the larger number of acid molecules.

That we find such a large proportion of lecithin in these compounds is accounted for by its great molecular weight. If the molecular weight of the protein were 15,000,<sup>1</sup> its compound with four molecules of lecithin would contain over 17 per cent. of the latter.

Although we are not yet in a position to distinguish between these several compounds, it is nevertheless now necessary to make a distinction between the vitellin as it exists in the yolk, combined with lecithin, and the insoluble substance free from lecithin, which we have prepared and analyzed. As the designation vitellin has generally, if not always, been understood to apply to a protein substance, we suggest that this term be henceforth reserved for the protein, which in egg-yolk is united to lecithin and not to the compounds formed by their union, which may more properly be called lecithin-vitellin.

These considerations raise the question, are the preparations analyzed, vitellin, as defined above, or are they compounds of this protein with some other, at present unknown substance. Since the preparations yield paranuclein on digestion with pepsin, it appears highly probable that they contain paranucleic acid, but in less proportion than occurs in paranuclein.

To test this hypothesis we treated 10 grams preparation 5 with 100 cc. of N/10 potassium hydroxide solution, and after

<sup>1</sup> We have pointed out in a former paper (This Journal, 21, 486), the reasons which make it probable that the weight of the protein molecule may be about 15,000.

standing some time added enough 0.4 per cent. hydrochloric acid to neutralize the alkali and give an excess of acid equal to 0.2 per cent. of the solution. Pepsin was then intermixed and the solution digested at 40° for forty hours. After some time a voluminous precipitate separated from the nearly clear liquid. This was filtered out, washed thoroughly with water, and mixed with 45 cc. N/10 potassium hydroxide solution, which dissolved the precipitate and just neutralized its acid reaction to phenolphthalein. This solution was filtered perfectly clear and 45 cc. of N/10 hydrochloric acid were added, which threw out the paranuclein as a voluminous gelatinous precipitate. This was filtered out, washed thoroughly with water and with alcohol, and dried over sulphuric acid. This preparation, 6, weighed 2.38 grams. Another preparation of paranuclein was made by suspending 50 grams of preparation 5 in 0.2 per cent. hydrochloric acid, adding pepsin and, after digesting for twenty-four hours, adding more acid and pepsin and continuing the digestion twenty-four hours longer. The insoluble paranuclein was then filtered out, washed thoroughly with water and with alcohol, and dried over sulphuric acid. It weighed 15.7 grams.

Preparation 7:

The yolks of 120 eggs were mixed with an equal volume of saturated sodium chloride brine and the mixture was shaken with ether containing a little alcohol. A perfectly clear red-yellow ether-layer and a clear pale yellow aqueous layer soon separated. The ether was drawn off and the aqueous solution again shaken with ether, which caused a part of the proteid to become insoluble, rendering the solution opaque and gelatinous. After the ether had separated, the aqueous solution was dialyzed until free from chlorides, when it was filtered and the very voluminous precipitate was suspended in 4 liters of 0.2 per cent. hydrochloric acid and digested with 3 grams of pepsin. After twenty-four hours the solution was decanted from a large deposit of insoluble matter; the latter was mixed with about one-third its volume of 0.4 per cent. hydrochloric acid and the digestion continued forty-eight hours longer, whereby the amount of insoluble matter was much reduced. The latter was then filtered out and repeatedly extracted with alcohol until the evaporated alcoholic washings left no residue. This required a



large quantity of alcohol and more than a week of time. The residue, air dried, weighed 32 grams and formed preparation 8.

These preparations were then dried at  $110^{\circ}$  and analyzed, with results as follows:

## COMPOSITION OF PARANUCLEIN.

	6	7	8
Carbon .....	46.69	47.72	44.48
Hydrogen .....	6.77	6.80	6.52
Nitrogen .....	14.66	14.64	14.34
Sulphur .....	0.86	0.94	0.82
Phosphorus .....	3.29	2.52	4.19
Ash .....	1.89	5.01	3.43
P <sub>2</sub> O <sub>5</sub> in ash .....	0.83	2.47	1.61

Assuming that the yolk proteid and the paranuclein are both compounds of paranucleic acid, we should be able to calculate the composition of the protein substance in our preparations if we knew the composition of this acid. Unfortunately we do not know this acid in the free state.

Liebermann and others have thought that paranucleic acid is identical with metaphosphoric acid, but we think it extremely improbable that metaphosphoric acid can exist in animal tissues.

In seeking to harmonize the analyses of paranuclein with those of the paranucleoproteid we find that they are brought into more or less accordance by reckoning them free from ash and from certain phosphoric acid radicals. Assuming that the hydrogen of the phosphoric acid is replaced by protein, we have "corrected" our analyses for the following phosphoric acids; *viz.*, HPO<sub>3</sub>, H<sub>2</sub>PO<sub>4</sub>, H<sub>3</sub>P<sub>2</sub>O<sub>7</sub>, and H<sub>4</sub>PO<sub>6</sub> by subtracting from the ash its P<sub>2</sub>O<sub>5</sub> and to the remainder (the bases) adding the phosphorus and oxygen of the respective acids and, after deducting their sum from 100, recalculating these remainders to percentage statements.

Corrected for PO<sub>3</sub> we find no satisfactory agreement, as is shown by the following figures obtained by thus correcting the analyses of preparations 2 and 6.

	2	6
Carbon .....	52.68	50.86
Hydrogen .....	7.28	7.37
Nitrogen .....	16.57	15.97
Sulphur .....	1.08	0.94
Oxygen .....	22.39	24.86
	<hr/> 100.00	<hr/> 100.00

Correcting for the other three acids, however, we find a close agreement between all the analyses of the preceding preparations as is seen in the following tables :

COMPOSITION OF THE PARANUCLEOPROTEID AND THE PARANUCLEIN CALCULATED FREE FROM  $\text{PO}_4$  AND ASH.

	Paranucleoproteid.					Paranuclein.		
	1	2	3	4	5	6	7	8
Carbon....	52.67	52.89	52.59	53.14	52.57	52.54	53.17	52.12
Hydrogen..	7.37	7.30	7.42	7.40	7.40	7.60	7.57	7.64
Nitrogen ..	16.62	16.64	16.70	17.19	16.11	16.50	16.31	16.80
Sulphur...	1.15	1.09	1.03	1.10	1.06	0.96	1.05	0.96
Oxygen...	22.19	22.08	22.26	21.17	22.86	22.40	21.90	22.48
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

The agreement of these figures makes it plain that the paranuclein consists of one or more compounds of the protein (vitellin) containing a larger proportion of the same acid that exists in the paranucleoproteid from which it originated. These protein compounds with paranucleic acid are therefore analogous to those with the nucleic acid which we have obtained from the wheat embryo and described in the preceding paper.

If, as many seem to think, the paranucleic acid is not in fact  $\text{H}_3\text{PO}_4$ , it may be found to be either  $\text{H}_4\text{P}_2\text{O}_7$  or  $\text{H}_5\text{P}_3\text{O}_{10}$ . These acids differ in composition so little from  $\text{H}_3\text{PO}_4$  that we find nearly or quite as close agreement when the analyses are calculated free from either of them, as the following table shows, in which is given the result of calculating the analyses free from  $\text{P}_2\text{O}_5$  and ash.

COMPOSITION OF THE PARANUCLEOPROTEID AND THE PARANUCLEIN CALCULATED FREE FROM  $\text{P}_2\text{O}_5$  AND ASH.

	Paranucleoproteid.					Paranuclein.		
	1	2	3	4	5	6	7	8
Carbon .....	52.79	53.00	52.70	53.31	52.71	53.05	53.56	52.78
Hydrogen.....	7.39	7.32	7.44	7.42	7.42	7.69	7.63	7.74
Nitrogen.....	16.66	16.67	16.74	17.25	16.19	16.66	16.43	17.02
Sulphur .....	1.15	1.08	1.03	1.10	1.06	0.98	1.05	0.97
Oxygen.....	22.01	21.93	22.09	20.90	22.62	21.62	21.33	21.49
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Considering the great differences in phosphorus-content of these preparations, the striking agreement of the analyses thus

calculated makes probable that the acid combined with the protein has nearly the composition  $H_3PO_4$  and contains little, if any, organic matter, or else contains an organic radical, whose composition is very nearly like that of the protein itself.

It may possibly be a methyl or ethyl phosphoric acid or some other quite simple organic phosphoric acid, but probably not so complex an acid as glycerophosphoric, as we have found a wide difference between the analyses when corrected for this acid.

It seems probable in view of these facts that further study will lead to the isolation and positive identification of this acid.

#### CONCLUSION.

Sodium chloride solutions dissolve from egg yolk a large amount of protein matter which has the properties of a globulin, being precipitated by diluting or dialyzing its solutions.

The substance soluble in salt solution consists of a mixture of compounds of protein matter with lecithin. Preparations of these compounds contain from 15 to 30 per cent. of lecithin. The more soluble products obtained by fractional precipitation contain larger proportions of lecithin than the less soluble; that is, they are more acid compounds. These compounds might well be called lecithin-nucleovitellin.

The lecithin thus combined is not removed by ether, but readily by alcohol. The insoluble lecithin-free proteid, obtained by treating the lecithin compounds with alcohol, has a constant composition when obtained from successive fractional precipitations of the lecithin compound. The following is the average of five accordant analyses representing fractional precipitations of the substance :

#### COMPOSITION OF NUCLEOVITELLIN.

Carbon .....	51.24
Hydrogen .....	7.16
Nitrogen .....	16.38
Sulphur .....	1.04
Phosphorus .....	0.94
Oxygen .....	23.24
	<hr/>
	100.00

This substance on digesting with pepsin yields paranuclein of variable composition. When the analyses of the nucleovitellin

and the paranuclein are calculated free from phosphoric acid,  $H_3PO_4$ , possibly identical with "paranucleic acid", the composition found for the organic part of all of these preparations is so nearly the same as to show that the proteid and the nuclein are both compounds of one and the same proteid body, vitellin, with a phosphoric acid, possibly  $H_3PO_4$ ,  $H_2P_2O_7$ , or some very simple organo-phosphoric acid. The composition of the organic part of the preparations calculated free from  $H_3PO_4$  gives as the average for eight preparations of the paranucleoproteid and the paranuclein, the following figures :

## COMPOSITION OF VITELLIN,

Carbon .....	52.71
Hydrogen .....	7.46
Nitrogen .....	16.64
Sulphur .....	1.05
Oxygen .....	22.14
	<hr/>
	100.00

THE PROTEIN CONSTITUENTS OF EGG WHITE.<sup>1</sup>

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received June 16, 1900.

A RECENT paper by the writer<sup>2</sup> gave an account of preparations of crystallized egg albumin which justified the conclusion that with the substance commonly called ovalbumin there is associated one or more other protein bodies, the properties of which were not definitely ascertained.

We have since repeated this work on a larger scale and have not only confirmed the former observations, but have obtained much additional information respecting these other protein bodies.

## FRACTIONAL PRECIPITATION OF EGG WHITE.

Six liters of the whites of freshly laid eggs were gradually and carefully mixed with an equal volume of saturated ammonium sulphate solution and formed the precipitate, A, which was filtered off.

To the filtrate saturated ammonium sulphate solution was

<sup>1</sup> From advance sheets of the report of the Connecticut Agricultural Experiment Station for 1899, communicated by the authors.

<sup>2</sup> Report Conn. Agr. Exp. Station for 1898, and this Journal, 21, 486.

added until a small permanent precipitate was produced, and then a mixture of 600 cc. of saturated ammonium sulphate solution, 830 cc. of water, and 27 cc. of concentrated hydrochloric acid were gradually added. After standing over night, the large quantity of fine needle-shaped crystals which separated, fraction B, was filtered out.

The filtrate, mixed with saturated ammonium sulphate solution until a small precipitate again formed, was allowed to stand over night, during which time another crystalline precipitate, C, separated.

By treating the filtrate from C in the same manner, another precipitate, D, was obtained, which consisted wholly of spheroids.

All the protein matter which remained in the filtrate from D was precipitated by saturating the solution with ammonium sulphate, and this made preparation E. These several fractions were then further divided as follows:

*Precipitate A* was treated with water, strained with difficulty, owing to its gummy character, through bolting-cloth, and the slightly turbid solution thus obtained was dialyzed for several days. The considerable mucin-like precipitate which separated was filtered out, washed with much water, and dehydrated with absolute alcohol, giving 26.88 grams of preparation A.1.a.

The filtrate from the precipitate of A.1.a., saturated with ammonium sulphate, yielded a precipitate which was treated with a little water, and the part insoluble therein filtered out; the filtrate was allowed to evaporate until an amorphous precipitate separated. This precipitate was filtered out, united with the insoluble part of the ammonium sulphate precipitate, dissolved in water, and its solution dialyzed, yielding a precipitate which resembled that previously obtained by dialysis, being largely composed of gummy, mucin-like clots. This, when well washed with water and alcohol and dried, gave 7.28 grams of A.1.b. The dialyzed solution from which A.1.b had separated, when treated with ammonium sulphate, yielded a precipitate which was filtered out, pressed on filter-paper, dissolved in water and this solution dialyzed free from sulphate. This dialyzed solution, evaporated at 40°, left a residue, marked A.2, weighing, dry, 16 grams.

The solution containing sulphate of ammonium, from which had been separated the substance yielding the two last-named preparations, was further concentrated by gradual evaporation, and yielded a mass of needle-shaped crystals. These were separated by filtration, dissolved in water, the solution was dialyzed till free from ammonium sulphate and evaporated at  $40^{\circ}$ , giving preparation A.3, weighing 11.56 grams.

*Precipitate B.*—This, consisting wholly of well-formed crystals, was dissolved in water and treated with saturated ammonium sulphate solution, which was added until precipitation began. After standing over night, the wholly crystalline precipitate was filtered out and the filtrate, marked b.2, treated as will be described later. The precipitate was again dissolved in water and enough ammonium sulphate added to give a precipitate from which, after a time, the solution was decanted. After pressing out the mother-liquor, the precipitate was dissolved in water and the clear solution dialyzed until wholly free from sulphate, when it was evaporated at  $50^{\circ}$ , giving 36 grams of B.1.

The filtrate from the precipitation of B.1 treated with more ammonium sulphate, on standing twelve hours, deposited a large crop of finely developed crystals. This was filtered out and, treated in the manner described for B.1, gave 59 grams of B.2. The filtrate from B.2 was added to solution b.2.

*Precipitate C.*—The filtrates from B.1 and B.2, forming solution b.2, were united with the aqueous solution of fraction C, ammonium sulphate was added to incipient precipitation and the mixture was allowed to stand over night. The substance, which separated in spheroids, was filtered out, dissolved in water and recrystallized by adding ammonium sulphate. On standing, the substance deposited in large aggregates of crystals, extending from the bottom of the dish in warty masses, some of them more than 2 cm. long and 0.5 cm. in diameter. These masses were wholly composed of exceptionally large and well-formed needle crystals. After separating from the mother-liquor, this crystalline mass was dissolved in water and the solution dialyzed till free from sulphate, and, evaporated at  $50^{\circ}$ , gave 45 grams of C.1.

The filtrate from C.1, on standing, yielded a very large quantity of substance which was composed almost wholly of crystals, only a very few spheroids being detected among them. This

precipitate, by the treatment applied to C.1, yielded 106 grams of C.2.

The filtrate from the first precipitation of C.1 was treated with more ammonium sulphate, the filtrate from C.2 was added, and the mixture allowed to evaporate slowly until a precipitate separated, which consisted of a mixture of crystals and spheroids. This yielded C.3, weighing 32.5 grams.

*Precipitate D.*—This was dissolved in water, ammonium sulphate solution was added and the mixture allowed to stand until a considerable separation of spheroids occurred, which, on settling, formed a clear, transparent deposit on the bottom of the dish.

After several reprecipitations, always without obtaining crystals, and thinking that the absence of crystals might be due to a deficiency of acid, we added to the solution 3 cc. of concentrated hydrochloric acid mixed with much ammonium sulphate solution. On standing, however, this solution, as before, deposited only spheroids. The deposit, after decanting the solution, was dissolved in water and its solution, after adding ammonium sulphate to incipient precipitation, was allowed to evaporate slowly. When considerable deposit had formed, the solution was decanted and allowed to concentrate until nearly all the remaining proteid matter had formed a coherent deposit of spheroids. These two deposits were each separately dissolved in water, their solutions dialyzed free from ammonium sulphate and evaporated to dryness at 50°, thus giving D.1, weighing 30 grams and D.2, weighing 20 grams.

The solution, decanted from the first precipitate which separated after adding acid, gave on evaporation a precipitate consisting wholly of spheroids, which formed D.3, weighing 55 grams. The solution from this, on further concentration, deposited nearly all the dissolved protein in the form of spheroids, which, by the usual treatment, gave 10 grams of D.4.

*Precipitate E.*—This, when dissolved in water, yielded a brilliant yellow solution, slightly acid to litmus. Thereto saturated ammonium sulphate solution, containing 1 cc. of concentrated hydrochloric acid, was added, which, on standing, caused a precipitate. This was filtered off, dissolved in water, ammonium sulphate was added to incipient precipitation, and after standing

seven days, the deposit of spheroids which had separated was filtered out, yielding 6.2 grams of E.1. The filtrate contained no protein matter.

The filtrate from the first reprecipitation of E was mixed with ammonium sulphate until a considerable amorphous precipitate had formed. This was filtered out, dissolved in water, and after adding ammonium sulphate and allowing the solution to stand six days, it gave a precipitate of spheroids which yielded E.2, weighing 15.65 grams.

The solution decanted from the first precipitation of E.2, after evaporating for six days, gave a deposit of spheroids mixed with a little amorphous matter, which was marked E.3, and weighed 22.5 grams.

We thus obtained from 6 liters of egg white, seventeen different fractions, containing 504 grams of substance, 262 grams of which were wholly crystalline, and since at least one-half of C.3 consisted of crystals, the total amount of crystalline matter was 278 grams. Evidently more than one-half the protein constituents of egg white can be crystallized. The yield of crystallized albumin was about the same as that obtained by the writer in his previous investigation, being about 4.4 grams of crystallized albumin per 100 cc. of egg white, as against 5.3 and 4.9 grams previously obtained.

*Fractions E.2 and E.3.*—Since the fractions E.2 and E.3 appeared, by their behavior on heating with water, to contain at least three protein substances, the greater part of each preparation was treated with water. E.2 contained some matter insoluble in water which could not be filtered out, while E.3 gave a clear solution. Both solutions, heated in a water-bath, gave a flocculent coagulum at 58° which, even after heating at 65° for some time, could not be filtered out. The temperature was therefore raised to 72° and held there some time, which caused more coagulum to separate in both solutions, but as the solutions could not even then be filtered, the bath was heated to boiling. With the rising temperature the coagulum rapidly increased, so that it could soon be filtered out on cloth. After thoroughly washing each coagulum with hot water and alcohol and drying over sulphuric acid, we obtained preparations E.2.a, weighing 6 grams, and E.3.a, weighing 8.6 grams. The clear, bright,



yellow filtrates from these were united and poured into several volumes of alcohol, which threw out a white precipitate and held the yellow coloring-matter in solution.

The precipitate, E.4, washed with alcohol and ether and dried over sulphuric acid, weighed 5 grams.

These preparations were then dried to constant weight at  $110^{\circ}$  and analyzed.

The heat coagulation points of their solutions, containing 2.5 per cent. of the protein substance and 10 per cent. of sodium chloride, were determined by gradually heating in a water-bath. In Table I, page 428, T indicates the temperature at which the solution first became turbid, and F that at which flocks separated.

The specific rotation was determined with a Schmidt and Haensch polarimeter, the readings on the sugar scale being converted into degrees of circular polarization by multiplying by 0.346.

In the table the percentages of nitrogen marked K, were found by the Kjeldahl process, those marked A, by the Dumas or absolute method.

These results entirely confirm those given in our former paper, but in consequence of the more extended series of fractional precipitations in the work now under discussion we have plainer evidence of the presence of the several protein constituents of the egg white.

Of these fractions, B.1, B.2, C.1, and C.2 consist of ovalbumin, separated in a completely crystalline condition, and, with the exception of a trace present in C.2, are wholly free from the lower coagulating albumin, thus demonstrating this latter to be a distinct substance. The rotation and elementary composition of these fractions are essentially the same as that given in our former paper for similar products.

In fraction E.4 we have ovomucoid not coagulated by heat, with a specific rotation of  $61.5^{\circ}$  and of the same composition as Möner<sup>1</sup> and Zanetti<sup>2</sup> found for this substance. The successive fractions, from C.3 to E.3.a inclusive, all have a higher specific rotation and contain a relatively considerable amount of an albumin coagulating at a much lower temperature than ovalbumin.

<sup>1</sup> *Ztschr. physiol. Chem.*, 18, 525.

<sup>2</sup> *Ann. di Chim. e Farmac.*, No. 12, 1897.

TABLE I.—THE WEIGHT, ROTATION, COMPOSITION, AND HEAT COAGULATION TEMPERATURES OF THE FRACTIONAL PRECIPITATES OF EGG WHITE.

Preparation.	Weight Grams.	[α] <sub>D</sub> .	Calculated ash-free.					Ash.	Coagulation temperature.	Remarks.
			C.	H.	N.	S.	P.			
A.1.a.	26.88	−21° 9'	50.69	6.71	14.49	2.280	trace	0.53	T 70° F 75°	Coagulum nearly disappears on boiling and reappears on cooling.
A.1.b.	7.28	. . .	50.95	6.85	14.82	1.938	none	1.41	. . .	
A.2.	16.00	−31° 50'	52.76	7.12	15.48K 15.58K	1.687	0.123	0.41	T 64° F 70°	Practically all coagulated above 70°.
A.3.	11.56	. . .	52.40	7.12	15.77K 15.66K	1.729	0.002	0.28	T 66° F 70°	
B.1.	36.00	−29° 53'	52.59	7.10	15.59K 15.51K	1.613	0.126	0.136	T 70° F 71°	None coagulated below 70°.
B.2.	59.00	−29° 13'	52.78	7.09	15.54K 15.60A	1.619	0.127	0.150	T 68° F 70°	None coagulated below 68°.
C.1.	45.00	−30° 2'	52.75	7.31	15.57A 15.43K	1.613	0.131	0.350	T 69° F 71°	None coagulated below 69°.
C.2.	106.00	−30° 48'	52.79	7.00	15.57K 15.63A	1.634	0.126	0.20	T 62° F 65°	Only a trace coagulated at this temperature. The rest separated at 70° and above.
C.3.	32.40	−34° 2'	52.24	7.08	15.55A	1.755	0.085	0.290	T 57° F 57°	Considerable coagulated below 70°, but most above 70°.
D.1.	30.00	−34° 18'	52.41	6.93	15.57A	1.796	0.106	0.14	T 51° F 53°	Much coagulated below 70°, but most above 70°.
D.2.	20.00	−37° 14'	52.29	6.94	15.61A	1.886	0.062	0.04		
D.3.	55.00	−41° 22'	51.62	6.94	15.23A 15.27K	1.972	0.048	0.10	T 52° F 55°	About 50 per cent. coagulated below 60°, about 35 per cent. at 70° and above. The rest did not coagulate.
D.4.	10.00	−51° 30'	50.56	6.80	13.64A 13.54A	1.997 2.017	trace	0.11	T 62° F 64°	Aqueous solution on heating, formed a clear jelly. Salt solution coagulated at 64°, and above. Much uncoagulated.
E.1.	6.20	−33° 36'	51.91	6.94	15.02A 15.27K	1.700 1.710	trace	0.49	T 59° F 60°	Probably about 40 per cent. was coagulated below 70°, much above 70°.
E.2.	15.65	−43° 7'	. . .	. . .	. . .	. . .	. . .	. . .	. . .	Less appeared to coagulate below 70° than of E.1 when heated in water with no salt.
E.3.	22.50	−49° 5'	. . .	. . .	. . .	. . .	. . .	. . .	. . .	Less separated below 70° than of E.2 when heated in water.
E.2.a.	6.00	. . .	52.40	6.91	15.69A	1.780	0.090	0.66	. . .	Not much separated below 70° when heated in water.
E.3.a.	8.60	. . .	51.94	6.84	15.31A	1.629	0.045	0.36	. . .	Not much separated below 70° when heated in water.
E.4.	5.00	−61° 34'	49.02	6.45	12.71A	2.379	0.11	0.750	. . .	No coagulum.

The fractions C.3, D.1, and D.2 have nearly the same rotation temperatures of coagulation and composition. We therefore subjected these to fractional precipitation, in order to determine whether they were mixtures of different proteids or were essentially one substance. The greater parts of these preparations were accordingly united, dissolved in about 400 cc. of water and saturated ammonium sulphate solution added, until a decided precipitate had formed. This was filtered out, freed from mother-liquor, dissolved in water, the solution dialyzed until free from ammonium sulphate and then evaporated to dryness below 50°. The residue, F.1, weighed 7.5 grams. The filtrate from F.1, on evaporating at the room temperature, deposited a quantity of spheroids, mixed with a few crystals of ovalbumin. This deposit was filtered out, dissolved in water, to the solution saturated ammonium sulphate solution was added until incipient precipitation set in, and the whole was allowed to stand until a considerable precipitate composed of spheroids mixed with a few crystals had formed. This was filtered out and, in order, if possible, to convert the whole into crystals, the original reaction of the egg white was imitated by making the aqueous solution of the precipitate slightly alkaline with ammonia. A very small excess of hydrochloric acid was added and then ammonium sulphate to incipient precipitation, thus reproducing, as closely as we could, the conditions under which the first crystalline separation had been obtained. After standing, a precipitate formed which contained no crystals. This was filtered out and, by the usual treatment, gave F.2, weighing 18.32 grams. The solutions filtered from the two preceding precipitations of F.2 were saturated with ammonium sulphate, and the resulting precipitate dissolved in water; its solution, dialyzed and evaporated below 50°, gave F.2.a, weighing 7.83 grams. The filtrate from the first precipitation of F.2 on further evaporation gave a precipitate of spheroids which was dissolved in water, and by the treatment employed for separating F.2.a, gave 16.7 grams of F.3.

The solution filtered from the second precipitation of F.3 was saturated with ammonium sulphate and from the precipitate produced by the usual treatment, F.3.a, weighing 5.38 grams, was obtained. These several preparations were found to have the

rotation, heat-coagulation temperatures and compositions given in Table II.

While none of these fractions was obtained free from the lower coagulating albumin, the relative proportions of the two albumins which the different fractions contained varied greatly, which fact, in conjunction with their rotation and composition, shows that a decided, though incomplete, separation has been effected.

In order to separate more completely the proteids which these mixed fractions appeared to contain, we dissolved 13.4 grams of D.3 in 500 cc. of 10 per cent. brine, and heated the filtered and perfectly clear solution slowly in a large water-bath. A flocculent coagulum began to separate at 52°, which, after heating for some time at 60°, was filtered off. The filtrate was then removed and this coagulum was washed with pure water, which, after the salt was removed, dissolved the coagulum almost completely. From these washings the proteid was separated by adding alcohol. When dried over sulphuric acid it weighed 5 grams and formed preparation D.3.1.

The solution filtered from the coagulum separating below 60°, when further heated, became turbid at 64° and yielded a flocculent coagulum at 70°. This second coagulum was filtered off after heating for some time at 88° and when washed and dried gave 3.5 grams of D.3.2. The filtrate from this gave no more coagulum on heating and after dialyzing free from chlorides was concentrated to small volume and precipitated by pouring into alcohol. This gave us 2 grams of D.3.3.

Seven grams of F.3 were dissolved in 280 cc. of 5 per cent. brine and the solution heated to 67°. The flocculent coagulum, which began to separate at 59°, was filtered out, washed and dried, giving 1.87 grams of F.3.1. The filtrate heated to 92° gave another coagulum which began to separate at about 70°. This, when dry, weighed 2.17 grams, F.3.2. The filtrate from F.3.2 dialyzed free from chlorides and, precipitated by alcohol, gave 1.39 grams of F.3.3.

Twenty-five grams of K.3 (the more soluble part of a precipitate obtained by adding an equal volume of saturated ammonium sulphate solution to a large quantity of egg white) were dissolved in about 800 cc. of 10 per cent. brine, the solution

TABLE II.—COMPOSITION, ETC., OF FRACTIONAL REPRECIPITATIONS OF THE INTERMEDIATE FRACTIONS OF  
TABLE I.

Prep.	Weight grams.	[α] <sub>D</sub> .	Ash free.						Coagula- tion tem- perature.	Remarks.
			C.	H.	N.	S.	P.	O.		
F.1.	7.50	36°4'	52.01	7.03	15.77D	1.768	0.069	23.353	0.36 { T 58° F 64°	First coagulum small, above 70° more than in F.2.a.
F.2.	18.32	32°2'	52.36	6.95	{ 15.59K 15.43K	1.689	0.117	23.374	0.47 { T 68° F 68°	Only a trace below 70°; much above 70°.
F.2.a.	7.83	38°35'	51.54	6.94	{ 15.19K 15.22K	{ 1.920 1.900	0.081	24.319	0.60 { T 60° F 63°	Considerable below 65°; above 70° more than in F.3.a.
F.3.	16.70	40°11'	51.32	6.72	15.34K	{ 1.782 1.810	0.009	24.815	0.32 { T 58° F 59°	Below 67°, nearly 35 per cent.; at 70° and above, nearly 40 per cent. coagu- lated.
F.3.a.	5.38	44°25'	51.29	6.77	15.30D	2.025	0.027	24.588	1.06 { T 62° F 64°	More below 65° than in any of these fractions of F.

filtered clear and heated to  $60^{\circ}$ . The coagulum was washed with salt solution, suspended in water after passing through fine bolting-cloth to break up all lumps, washed thoroughly with water, and with alcohol, and was dried, giving 2.78 grams of K.3.1. Unlike ovalbumin, this coagulated proteid separated in a finely divided state, so that it could be easily washed through the cloth.

The filtrate from this coagulum was dialyzed free from chlorides and then evaporated to dryness below  $60^{\circ}$ , leaving a residue which weighed 17.2 grams and had a specific rotation of  $37^{\circ} 55'$ . This rotation being much greater than that of ovalbumin, the whole of this residue was dissolved in 10 per cent. brine, the solution heated in a boiling water-bath, the coagulum, K.3.2, filtered off, the filtrate dialyzed free from chloride, and the clear solution poured into alcohol. The substance, K.3.3, thus precipitated, weighed, dry, 1.39 grams, and consisted of ovomucoid as shown by its rotation,  $61^{\circ} 30'$ .

The preparation, K.3, was prepared from the precipitate produced by half saturating the egg white solution with ammonium sulphate, which precipitate is commonly supposed to consist almost wholly of globulin. Nevertheless our results show that K.3 contained about 11 per cent. of the albumin coagulating below  $65^{\circ}$ , 83 per cent. of ovalbumin, and over 5 per cent. of ovomucoid. That so much of this latter substance should be present in this preparation is surprising and shows the difficulty in separating ovomucoid from ovalbumin.

All these preparations were analyzed with the results given in Table III.

These figures show that an albumin coagulating at  $55^{\circ}$ – $57^{\circ}$  forms nearly 50 per cent. of the products obtained from D.3. This albumin contains somewhat less carbon, decidedly more nitrogen, and a little more sulphur than ovalbumin. Since it so closely resembles ovalbumin, and is so intimately associated with it the writer suggests that it be called *conalbumin*. The rest of the products from D.3 consists of about 35 per cent. ovalbumin and 18 per cent. ovomucoid. From F.3, 27 per cent. of conalbumin, 31 per cent. of ovalbumin, and 20 per cent. of ovomucoid were obtained.

This investigation of the protein constituents of the egg white

TABLE III.—COMPOSITION, ETC., OF PRODUCTS DERIVED FROM FRACTIONS D, F, AND K.											
Prepara- tion.	Weight, Grams.	[α] <sub>D</sub> .	Ash free.						Coagula- tion tem- perature.	Remarks.	
			C.	H.	N.	S.	P.	O.			Ash.
D.3.1.	5.00	....	52.19	6.84	16.10K	1.67	0.010	23.19	0.85	{ T 48° F 52°	Formed about 48 per cent. of D.3.
D.3.2.	3.81	....	52.08	7.04	15.36	1.61	0.110	23.80	0.23	{ T 64° F 70°	Formed about 35 per cent. of D.3.
D.3.3.	2.00	61°10'	48.90	6.61	12.16K	2.34	none	29.99	2.33	{ ....	No coagulum. Formed about 18 per cent. of D.3.
F.3.1.	1.87	....	....	....	{ 16.03K 16.15K	17.3	trace	....	1.19	{ T 58° F 59°	Formed about 27 per cent. of F.3.
F.3.2.	2.17	....	....	....	15.16K	1.61	....	....	2.00	{ T 70° F 70°	Formed about 31 per cent. of F.3.
F.3.3.	1.39	61°20'	....	....	....	....	....	....	....	{ ....	No coagulum. Formed about 20 per cent. of F.3.
K.3.1.	2.78	....	52.31	7.05	16.16K	1.71	trace	22.77	0.56	{ T 57° F 60°	Formed about 11 per cent. of K.3.
K.3.3.	1.39	61°30'	....	....	....	....	....	....	....	{ ....	Formed about 5.5 per cent. of K.3.

shows them to be ovomucin, ovalbumin, conalbumin, and ovomucoid. These have the following properties :

*Ovomucin* is a glycoproteid recently discovered by Eichholz<sup>1</sup> to be present in small amount in egg white. This substance, precipitated by diluting egg white, has heretofore been regarded as globulin, but we find that nearly, if not quite, all of that which is so precipitated, is ovomucin.

From the whites of 240 eggs we obtained, although with some loss, 34.2 grams of ovomucin or about 7 per cent. of the proteid matter of the egg white, which is the proportion in which Dillner found the "globulin" to be present.

When freshly precipitated by dilution or dialysis, ovomucin loses its gummy character on thoroughly washing with water, but, when treated with salt solutions, forms a transparent gummy mass, which, on agitation, yields a clear but viscid solution.

When washed with alcohol and dried, ovomucin forms a light, white powder, partly soluble in sodium chloride brine, and gives a solution free from viscosity, which becomes turbid at 75°, and yields flocks at 78°. On boiling, this coagulum almost wholly dissolves and reappears on cooling.

Eichholz states that ovomucin dissolves in dilute sodium carbonate solutions. We find, however, that when treated with much 1 per cent. sodium carbonate, only an apparent solution results, for, when this is brought into filters, a clear, thin liquid passes through the paper from which, by adding acid, only an insignificant precipitate can be obtained, while a clear and very viscid liquid, containing almost all the ovomucin, remains upon the paper.

We have made, page 423, two preparations of ovomucin which had the following composition :

OVOMUCIN.		
	A.I.a.	A.I.b.
Carbon .....	50.69	50.95
Hydrogen .....	6.71	6.85
Nitrogen .....	14.49	14.82
Sulphur .....	2.28	1.94
Oxygen.....	25.83	25.44
	<hr/> 100.00	<hr/> 100.00

<sup>1</sup> *Jour. of Physiology*, 23, 167.



*Ovalbumin* is the chief constituent of egg white, 50 per cent. of its proteids having been obtained in this investigation in the form of perfectly crystallized preparations of this substance, while a large proportion of the remaining proteid matter also consisted of this albumin.

*Heat Coagulum of Ovalbumin.*—Solutions in pure water, containing 2.5 per cent. of pure ovalbumin, become turbid at 60°, and at 64° yield a flocculent coagulum.

When 10 per cent. of sodium chloride is added to these solutions the temperature of coagulation becomes higher, turbidity developing at 69°, and flocks at 70°.<sup>1</sup>

When its solution is evaporated to dryness below 50°, and the ovalbumin redissolved in water or in brine, a small amount of substance coagulating at the lower temperature appears to be formed. Thus, sodium chloride solutions containing 2.5 per cent. of B.1, B.2, or C.1, before these substances had been separated by evaporation at 50°, remained absolutely clear until heated to 68° or 69°, while similar solutions, made by dissolving the dried substance, became turbid at 59° and yielded flocks in small quantity at 63°.

Preparations of ovalbumin obtained by evaporating their solutions in pure water to dryness below 50°, do not completely redissolve when treated with water.

Solutions of some preparations thus made, become very rapidly turbid when filtered and gradually deposit a not inconsiderable quantity of insoluble matter. The amount of insoluble matter in all of our preparations was so small, that we have been unable to learn its nature, but in one case we obtained 0.72 gram from 15 grams of a preparation containing a larger proportion than any we had seen before. This insoluble substance, which contained 15.65 per cent. nitrogen, and 1.8 per cent. sulphur, was probably a mechanical coagulum, as it tended to separate at points of contact between the surface of the albumin solution and the vessel containing it. Sodium chloride added to the solution in sufficient quantity diminishes the amount, or prevents its formation.<sup>2</sup>

<sup>1</sup> Stärke (Pflüger's *Archiv.*, 12, 18) notes this effect of sodium chloride on the coagulation of the albumin.

<sup>2</sup> See Hopkins: *Jour. of Physiology*, 25, 324.

It has been stated by Hammarsten that with a constant amount of salt the temperature of coagulation changes with variable amounts of albumin in solution.

We, accordingly, prepared solutions of the dialyzed, but not dried, albumin which contained 5, 2.5, and 1.0 per cent. of ovalbumin and also similar solutions containing, in addition, 10 per cent. of sodium chloride. These, when heated very slowly in a large water-bath, coagulated as follows :

		Water.	10 per cent. salt solution.
5.0 per cent. albumin	turbidity.....	59°	68°
	flocks.....	64°	71°
2.5 " " "	turbidity.....	60°	69°
	flocks.....	64°	71°
1.0 " " "	turbidity.....	61°	69°
	flocks.....	67°	71°
0.5 " " "	turbidity.....	63°	..
	flocks.....	none even on boiling.	

These figures show no difference in temperature of coagulation, for solutions containing from 1 to 5 per cent. of ovalbumin, together with 10 per cent. of sodium chloride, but solutions of ovalbumin in pure water coagulate at a lower temperature than those containing 10 per cent. of this salt; those containing 5 and 2.5 per cent. of albumin, coagulate at one and the same temperature; those containing 1 per cent. coagulate somewhat higher, while a solution containing but 0.5 per cent. of albumin yields no flocks even on boiling.

When the proportion of albumin remains constant, while that of the salt increases, the temperature of coagulation rises, as the following table shows :

NaCl. Per cent.	Ovalbumin. Per cent.	
1.0	2.5	{ 61° turbidity. 63° flocks.
3.0	2.5	{ 63° turbidity. 65° flocks.
5.0	2.5	{ 65° turbidity. 67° flocks.
10.0	2.5	{ 68° turbidity. 70° flocks.

From these results we may state that solutions in water which contain from 2.5 to 5 per cent. of pure ovalbumin become turbid on heating to 60°, and yield a flocculent coagulum at 64°,

while those containing, in addition, 10 per cent. of sodium chloride become turbid at 68°, and flocculent at 70°.

In the preceding experiments no acid was added to the solution to be coagulated, the acidity of the ovalbumin (1 gram of albumin required 2 cc. of N/10 alkali for neutralization to phenolphthalein) being sufficient to bring about coagulation.

When the albumin was exactly neutralized to phenolphthalein, by adding potash, the solution remained clear when heated for some time at 100°. When this solution was treated with acid equivalent to the added alkali a large precipitate resulted which did not separate completely until a very slight excess of acid was added. Thus, when 0.5 gram of albumin was dissolved in 19 cc. of water, 1 cc. N/10 potassium hydroxide added, making the solution exactly neutral to phenolphthalein, and the mixture heated for ten minutes in boiling water, no coagulum was produced. When cooled, 1 cc. of N/10 hydrochloric acid was added, which gave a precipitate, from which a clear filtrate could not be obtained; with 1.2 cc., however, the precipitation was so complete that the filtrate gave no turbidity with alcohol. When 1 gram of albumin was dissolved in water and 2 cc. of N/10 ammonia solution were added, a quantity just sufficient to neutralize the acid reaction of the albumin, the solution remained clear after heating for some time at 100°. After cooling, on adding N/10 hydrochloric acid, the solution remained clear until nearly enough acid had been added to neutralize the 2 cc. of ammonia, but when the full 2 cc. were added the albumin was so completely precipitated that the solution filtered from the coagulum contained only a trace of protein matter. The solution, thus neutralized with either potash or ammonia, gave off hydrogen sulphide when heated and acidified.

To six tubes, each containing 0.5 gram of albumin, dissolved in 10 cc. of water, were added respectively 0.2, 0.4, 0.6, 0.8, 1, and 1.1 cc. N/10 hydrochloric acid, and then water enough to make each up to 20 cc. When these mixtures were heated in boiling water, the one with 0.8 cc. of acid yielded some coagulum, that with 1 cc. but a trace, while that with 1.1 cc. remained clear, showing 1 cc. of N/10 hydrochloric acid to be enough to convert 0.5 gram of albumin into a compound not coagulated by heat. The portions with 0.2 and 0.6 cc. were com-

pletely, while that with 0.8 cc. was incompletely, coagulated. When 0.5 gram of albumin was dissolved in 20 cc. of water, containing from 0.5 cc. to 3 cc. of N/10 acetic acid and heated in a boiling water-bath, the albumin was practically completely coagulated; with 5 cc. of acetic acid the solution became opalescent at 64°, and formed a firm, transparent jelly at 75°. On heating at 99° with 10 cc. of N/10 acetic acid the solution formed a clear, thin jelly.

When solutions in pure water of any of our purest preparations of ovalbumin were heated to boiling for some time the albumin was so incompletely coagulated that a clear filtrate could not be obtained.

Six 2-gram portions of pure ovalbumin, were dissolved, each in 100 cc. of water, and mixed with equal volumes of water, containing 1, 2, 3, 4, 5, and 6 cc. of N/10 acetic acid respectively, and the mixtures boiled and poured on filters. The portion with 1 cc. of acid clogged the filter, as the coagulum separated imperfectly, whereas the others yielded clear filtrates. These, when evaporated to dryness, left residues weighing 0.0492, 0.0332, 0.0320, 0.0446, and 0.0648 gram, respectively.

From this it is seen that with 1 cc. of N/10 acetic acid the coagulation is incomplete, while with 3 and 4 cc. the amount of matter remaining in solution is less than with 2 cc. or than with 5 and 6 cc. This dissolved matter, which is very soluble in water, yields a solution decidedly acid to phenolphthalein and to litmus, contains proteid, and reduces Fehling's solution. Since the proportion, in which it is produced, appears to depend upon the quantity of acid added, we are inclined to regard it chiefly as a product of the action of the added acid upon a small part of the albumin, whereby uncoagulable acid compounds are formed in small, but variable proportion.

*Specific Rotation.*—This was determined for solutions of the ovalbumin in pure water, with a Schmidt and Haensch polarimeter, the readings of the sugar scale being converted into degrees of circular polarization by multiplying by 0.346, and the amount of dissolved albumin ascertained by evaporating and drying the residue at 110°. Preparations B.1, B.2, C.1, and C.2 showed very nearly the same rotation as that found by us in our

former work for preparations of pure ovalbumin. These determinations gave the following values for  $[\alpha]_D$ .

A.1 <sup>1</sup> .....	—29.31°	B.1.....	—29.53°
A.2 <sup>1</sup> .....	—29.40°	B.2.....	—29.13°
H.1 <sup>1</sup> .....	—28.60°	C.1.....	—30.03°
H.2 <sup>1</sup> .....	—29.81°	C.2.....	—30.80°

The degree of rotation was found to be the same in sodium chloride solutions as in water, and also to be the same for the albumin in the dialyzed solutions of the crystals, as in solutions of the albumin which had been separated from such solutions by evaporation at 50°.

Since this paper was written we have received the number of the *Journal of Physiology* issued April 24, 1900, containing a paper on "Pure Albumin", by F. G. Hopkins, in which he gives the rotary power of pure albumin as —30.70°. The remarkable agreement between the rotation of the many fractional crystallizations, obtained by Hopkins, is much closer than between those observed by us, which is probably due to his superior polariscope and to the stronger solutions of the albumin, containing considerable amounts of ammonium sulphate, which he employed. Because solutions rich in pure albumin, when free from salts, are not easily obtained absolutely clear and tend to become turbid, probably from mechanical coagulation, we were generally not able to use solutions so rich in albumin as those employed by Hopkins. The difference of 1.3° between the values of  $[\alpha]_D$  found by Hopkins and the writer, is probably chiefly due to the different methods employed for determining albumin in the solution examined. We have shown, page 438, that when ovalbumin is coagulated in the presence of a minimum of acetic acid, about 1.5 per cent. of uncoagulated matter remains in solution. Whether this occurs under the conditions under which Hopkins coagulated his albumin requires further investigation. Hopkins admits that the method employed by us is the more accurate, assuming that all ammonium sulphate can be separated from the albumin solution. We believe that we have accomplished this in view of the great care we have taken to detect the presence of sulphates in our albumin preparations and feel quite sure that we have not overlooked a quantity of ammo-

<sup>1</sup> These are preparations of the old series formerly described, and the two first are not parts of fraction A of the present series.

nium sulphate sufficient to have caused a difference of 4 per cent. of the observed rotation.

*Elementary Composition.*—In the following table we give the analyses of our four purest preparations of ovalbumin, and also analyses of two preparations made by Hofmeister's method as described on page 441.

COMPOSITION OF OVALBUMIN.							
	B.1.	B.2	C.1.	C.2.	No. 2.	No. 3.	Aver- age.
Carbon.....	52.59	52.78	52.75	52.79	52.82	52.78	52.75
Hydrogen...	7.10	7.09	7.31	7.00	7.03	7.07	7.10
Nitrogen....	15.55	15.57	15.50	15.60	15.32	15.53	15.51
Sulphur.....	1.613	1.619	1.613	1.634	1.590	1.651	1.620
Phosphorus .	0.126	0.127	0.131	0.126	0.123	0.112	0.122
Oxygen .....	23.021	22.814	22.696	22.850	23.117	22.857	22.898
	100.000	100.000	100.000	100.000	100.000	100.000	100.000

ANALYTICAL METHODS.

*Carbon and hydrogen* were determined by using an open tube with copper oxide, lead chromate, and metallic copper, and finishing the combustion in oxygen.

*Nitrogen* was determined by Dumas' method, the air being removed by a Sprengel pump, the tube then filled with carbon dioxide set free by heating sodium bicarbonate at the front end, again emptied by the pump and this process repeated. In this way all the air was removed and no fixed gas was driven off on heating the reagents. Nitrogen was also determined by the Kjeldahl method and results in close accord with those of Dumas' method were obtained.

*Sulphur* was determined by fusing about 1 gram of the substance with sodium hydroxide and peroxide over an alcohol lamp. The reagents were proved to be free from sulphur.

*Phosphorus* was determined by fusing about 1 gram of the substance with sodium peroxide, dissolving the fusion in nitric acid, precipitating with molybdic solution and weighing as magnesium pyrophosphate.

The figures given in the above table agree well with those of others who have prepared and analyzed ovalbumin with especial care as may be seen in the following table :

COMPOSITION OF OVALBUMIN.							
	C.	H.	N.	S.	P.	O.	
Hammarsten .....	52.25	6.90	15.25	1.64	...	23.69	uncoag.
Chittenden and Bolton....	52.33	6.98	15.89	1.83	...	22.97	"
" " .....	52.33	6.98	15.84	1.81	...	23.04	coag.
Bondzinski and Zoja.....	52.39	7.11	15.39	1.66	...	23.45	"
Osborne and Campbell....	52.75	7.10	15.51	1.62	0.12	22.90	
Hopkins.....	52.75	7.12	15.43	1.57			

There would be no longer any question about the composition of ovalbumin, were it not for Hofmeister's<sup>1</sup> analysis of a single preparation, and the recent assertion of Schulz,<sup>2</sup> that on crystallizing by the "acid process" a hydrate of Hofmeister's egg albumin is formed. This we have shown in our former paper to be untrue, for we there gave the results obtained by analyzing a preparation made exactly according to Hofmeister's method, which agreed quite well with the analyses of all our other preparations made by the acid method of Hopkins.

That there should be no question as to the composition of crystallized ovalbumin made according to Hofmeister's method we made preparation No. 2, recrystallized six times and coagulated by alcohol, No. 3, by recrystallizing four times, pressing the crystals on filter-paper, dissolving them in water, dialyzing the solution perfectly free from sulphate and evaporating the filtered solution at 50° to dryness.

Dried at 110° these preparations were found to have the following composition :

COMPOSITION OF OVALBUMIN CRYSTALLIZED BY HOFMEISTER'S METHOD.

	No. 2.	No. 3.	Average of the analyses given on page 365.
Carbon .....	52.82	52.78	52.75
Hydrogen .....	7.03	7.07	7.10
Nitrogen .....	15.32	15.53	15.51
Sulphur .....	1.590	1.651	1.62
Phosphorus.....	0.123	0.112	0.12
Oxygen .....	23.117	22.857	22.90
	<hr/> 100.000	<hr/> 100.000	<hr/> 100.000

These analyses are in almost exact agreement with the average given in the preceding table, and fail to confirm Hofmeister's figures for sulphur, or the conclusions drawn by him and by Schulz respecting the relation of the crystallized albumin to that heretofore obtained by other methods. The percentage of carbon found by us falls midway between that given by Hofmeister and the average of that given by the other investigators, with the exception of Hopkins. The very close agreement in composition between all the many fractions, having a constant rotatory power, analyzed by Hopkins and by ourselves, leaves

<sup>1</sup> *Ztschr. physiol. Chem.*, 16, 187.

<sup>2</sup> *Ibid.*, 29, 86.

little doubt as to the true elementary composition of crystallized ovalbumin, especially in view of the close agreement of these analyses with those of Hammarsten and of Bondzynski and Zoja.

In view of the statements recently made by Schulz concerning the proportion of sulphur in ovalbumin,<sup>1</sup> we used the very greatest care in determining this element. Our solutions of albumin were not only dialyzed until they gave no reaction with barium chloride, but until no sulphate could be detected in the water outside of the dialyzer, even after concentration. That our higher figures for sulphur are not due to ammonium sulphate, which could not be separated from the albumin by dialysis, is disproved, not only by the close agreement between our many analyses, but also by the fact that we obtained exactly the same figures from preparations free from conalbumin and ovomucoid, made by coagulating their dilute solutions at 70°–95°. Thus, we found in D.3.2, 1.61, in F.2.1, 1.64, in F.3.2, 1.61, and in E.3.a, 1.63 per cent. We have no doubt that these figures very closely represent the true proportion of sulphur contained in the ovalbumin, especially as they agree with the figures which Hammarsten obtained,<sup>2</sup> by four different methods; namely, 1.67, 1.67, 1.62, and 1.58 and also with those of Bondzynski and Zoja. The results obtained by Hopkins,<sup>3</sup> which have come to our notice since this paper was written, leave no doubt whatever that the true proportion of sulphur is very close to 1.60 per cent., Hopkins finding an average of 1.57 per cent. while we find 1.62 per cent., the slight difference between our results being doubtless due to slight differences in our methods of operation.

It is to be noted that we have found a small but uniform quantity of *phosphorus* in all our preparations of crystallized albumin. In Table I, page 428, it is seen that the four crystallized preparations, B.1, B.2, C.1, and C.2, all contained 0.12 per cent. of phosphorus, whereas all the other non-crystalline preparations contained less, the amount diminishing as the proportion of ovalbumin diminished in the successive fractions. In Table

<sup>1</sup> *Ztschr. physiol Chem.*, 28, 16; 29, 86.

<sup>2</sup> *Ibid.*, 9, 304.

<sup>3</sup> *Jour. of Physiology*, 28, 306.



III, page 432, it appears that D.3.1, consisting of conalbumin, contained but 0.01 per cent., whereas D.3.2, consisting of coagulated ovalbumin, contained 0.11 per cent., and D.3.3, consisting of ovomucoid, contained but a trace.

In our earlier series of preparations, this phosphorus was found in the ash, as calcium phosphate; in our present series, only a part of it was present in the ash, in which it occurred as sodium or potassium metaphosphate.

As our former series of preparations were dialyzed in river water containing calcium bicarbonate and our later series in distilled water, it seems highly probable that this phosphorus belongs to an acid united with the crystallized albumin in the same manner as the writer has shown that hydrochloric acid unites with edestin to form crystalline compounds.<sup>1</sup>

As to the nature of this phosphorized acid we have learned nothing, owing to the small proportion in which it is present.

#### THE CARBOHYDRATE SPLIT FROM THE OVALBUMIN BY BOILING WITH ACIDS.

These purest preparations of ovalbumin, which we have shown to have a constant specific rotation, the same composition and the same temperature of coagulation, when boiled with acids, all give solutions which yield considerable quantities of crystalline precipitates with phenylhydrazine.

When boiled with 3 per cent. hydrochloric acid for thirty minutes, the solution obtained reduces Fehling's solution, but fails to do so after boiling for three hours. The addition of Fehling's reagent to such solutions causes an intense biuret reaction, but no reduction of the copper salt takes place, even after adding considerable quantities of glucose. Evidently, by continued boiling, some substance is produced which prevents the reduction of the Fehling's solution. Blumenthal and Mayer<sup>2</sup> state that after long boiling this reduction is not so easily detected as after boiling for a short time.

Ten grams of each of the four preparations, B.1, B.2, C<sub>1</sub>, and C.2, were boiled with 200 cc. of 9 per cent. sulphuric acid for three hours and the solutions neutralized to litmus with baryta. The soluble matter was filtered out, washed with water, and the filtrate

<sup>1</sup> This Journal, 21, 486.

<sup>2</sup> *Ber. d. chem. Ges.*, 32, 274.

and washings were evaporated to a volume of 100 cc. To this solution 10 grams of sodium acetate were added and 5 cc. of a mixture of equal volumes of phenylhydrazine and 99 per cent. acetic acid, and the whole heated for three hours in boiling water. After standing over night, the crystalline precipitates were filtered off and washed rapidly with water and then with absolute alcohol, which removed a considerable quantity of deep red-colored, amorphous substance. The washed precipitates were then dried at  $110^{\circ}$  and weighed.

In order to learn the effect of the presence of ovomucoid, upon this precipitation with phenylhydrazine, 10 grams of G.4, which had a specific rotation of  $39^{\circ} 22'$ , and contained much ovomucoid, were treated in the same manner as these albumin preparations and at the same time with them.

For comparison, 100 cc. of a solution containing 1 gram of glucose were treated with phenylhydrazine under the same conditions. The filtrate from each phenylhydrazine precipitate was further treated with 5 cc. of phenylhydrazine and 10 grams of sodium acetate and a second precipitate obtained. From the filtrates from the second precipitations no more could be separated by further additions of phenylhydrazine. The weight of each precipitate dried at  $110^{\circ}$ , is given in the following table :

	B.1.	B.2.	C.1.	C.2.	G.4.	Glucose.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
1st . . . .	0.2019	0.1327	0.1831	0.0902	0.2175	0.3098
2nd . . .	0.1030	0.1027	0.0980	0.0281	0.2684	0.3187
	<hr/> 0.3049	<hr/> 0.2354	<hr/> 0.2711	<hr/> 0.1183	<hr/> 0.4859	<hr/> 0.6285

Since from C.2 we got so much less of this substance than from the others, we repeated this experiment, using for the first precipitation 10 cc. of the phenylhydrazine-acetic acid mixture and 20 grams of sodium acetate. In this way we got

C.2.		Gram.
1st . . . . .		0.1787
2nd . . . . .		0.0894
		<hr/> 0.3681

The crystals of the osazone obtained from the albumin consisted of feathery sprays and always appeared distinctly differ-

ent from the aggregates of needles yielded by glucose. Two different preparations of the phenylhydrazine compound were separately recrystallized by dissolving in boiling absolute alcohol, adding water, boiling until most of the alcohol had been expelled, and then allowing the solution to cool slowly until the substance separated in beautiful, yellow crystals of the same form as the original precipitate. These melted at  $187^{\circ}$  and  $189^{\circ}$ .

The amount of this osazone indicates that a considerable quantity of carbohydrate is split from our albumin preparations by boiling with acids. The quantity of osazone which we obtained from our preparations varied from one-third to one-half of that given by 1 gram of glucose under like conditions, and if the compound from the albumin is precipitated in the same proportion as the glucosazone we may infer that the albumin yields on hydrolysis from 3 to 5 per cent. of carbohydrate. The amount of osazone which we have actually obtained corresponds to from 2–2.5 per cent. of carbohydrate calculated as glucose. Hofmeister<sup>1</sup> obtained from 1 gram of ovalbumin 0.13 gram of osazone, from which he infers the presence of 15 per cent. of carbohydrate.

Does this carbohydrate come from the ovalbumin or from a residue of ovomucoid which we have not separated by our fractional crystallizations? Seemann<sup>2</sup> obtained a copper oxide reduction from ovomucoid corresponding to 34.9 per cent. of glucose. If this proportion is correct, we must have at least 6 per cent. of ovomucoid in our albumin preparations, to account for the minimum yield of osazone, corresponding to 2 per cent. of carbohydrate. This is probably the least quantity of ovomucoid which could yield this quantity of osazone. From the incompleteness of precipitation of osazone, it is probable that the quantity of ovomucoid would have to be more than twice as great to yield the quantity of osazone found. From G.4, which had a specific rotation of  $39^{\circ} 22'$ , we obtained nearly twice as much osazone as from the ovalbumin, due unquestionably to the presence of ovomucoid in this preparation. If this increased yield of osazone is attended by an increase of  $10^{\circ}$  in the rotation, an admixture of ovomucoid sufficient to yield such quantities of

<sup>1</sup> *Ztschr. physiol. Chem.*, 24, 170.

<sup>2</sup> *Archiv. f. Verdaunungskrankheit.* 4, 275.

osazone would manifest itself by variations in the rotation of these albumin preparations, it being improbable that so much ovomucoid was admixed in uniform proportion in the successive crystallized precipitates. We have shown on page 438 that the preparations of ovalbumin when coagulated by heat, left in solution a small quantity of uncoagulable matter amounting to about 1.6 per cent. of the albumin, the nature of which we have been unable to discover, owing to its small quantity. It may be ovomucoid, since it contains proteid matter and yields a copper-reducing body on boiling with acids, but in general appearance and manner of dissolving it does not behave like ovomucoid. As already stated on page 439, we think it more probable that this substance is a product of the action of acetic acid, whereby a small quantity of uncoagulable acid compounds of the albumin is formed. Hydrochloric acid, added in the same proportion as acetic acid, converts, in the absence of soluble salts, nearly all of the albumin into such uncoagulable compounds. A somewhat greater quantity of acetic acid does the same, entirely preventing coagulation. We therefore feel almost certain that the carbohydrate does not originate in admixed ovomucoid, but is derived from the substance constituting the crystallized ovalbumin.

This belief is strengthened by the fact that, so far as we know, all but two of the several investigators who have thus examined coagulated egg albumin, have found evidence of the presence of considerable quantities of carbohydrates among its hydrolytic decomposition products, although most of them have endeavored to separate every trace of ovomucoid. Spencer,<sup>1</sup> who failed to find carbohydrate, boiled his coagulated albumin for several hours with weak potash and then for thirty minutes with 10 per cent. potash, a procedure which might lead to the destruction of carbohydrate. Moerner<sup>2</sup> who also found no carbohydrate, gives no account of the method he used in preparing the ovalbumin.

Hammarsten regards crystallized ovalbumin as a glycoproteid and considers the carbohydrate group to be a constituent of a non-proteid substance combined with the protein substance proper.

<sup>1</sup> *Ztschr. physiol. Chem.*, 24, 354.

<sup>2</sup> *Centrbl. Physiol.*, 7.

This is certainly true of the nucleoproteid of the pancreas from which Bang obtained guanylic acid, which on hydrolysis yielded about 30 per cent. of carbohydrate. The mucins also appear to be compounds of protein matter with sugar-yielding substances.

We have stated our belief that crystallized ovalbumin is a compound of some acid with protein substance and consider it quite probable that this acid contains the carbohydrate group.

We have been unable to obtain any evidence of carbohydrate in edestin, the crystallized globulin of hemp-seed, nor, according to Hammarsten, can a carbohydrate be split from casein, vitellin, myosin, and fibrinogen. This subject requires further careful study before a definite conclusion can be reached. At present the preponderance of evidence indicates that the carbohydrate is not derived from the protein molecule, but from substances combined with the protein as it is obtained from the tissues or secretions.

*Conalbumin*.—Our fractions of the proteids of egg white obtained after separating the crystallized fractions, all have a higher rotation and sulphur content and a lower temperature of coagulation than ovalbumin, as is shown in Table I. In Table III we showed that these fractions could be separated into two products by heating their solutions to 65°, filtering off the coagulum, and then heating the filtrate to 90°. In the filtrate from this latter coagulum a substance remained which was not coagulated by boiling.

The body coagulating at the lower temperature we designate *conalbumin*, on account of its close relation in properties and composition to ovalbumin. What this relation may be, we have not determined. Conalbumin and ovalbumin may be different compounds of the same protein, or the former may be a derivative of the latter involving a molecular change.

#### COMPOSITION OF COAGULATED CONALBUMIN.

	D.3.1.		F.3.1.		K.3.1.		Average.
	I.	II.	I.	II.	I.	II.	
Carbon .....	52.17	52.20	....	....	52.47	52.14	52.25
Hydrogen ...	6.98	6.70	....	....	7.02	7.09	6.99
Nitrogen ....	16.04	16.16	16.03	16.15	16.16	....	16.11
Sulphur .....	1.67	....	1.73	....	1.71	....	1.70
Oxygen .....	23.14	....	....	...	22.64	....	22.95
	<hr/> 100.00				<hr/> 100.00		<hr/> 100.00

These figures show very little difference in composition between ovalbumin and conalbumin, the carbon being about 0.5 per cent. lower, the nitrogen about 0.53 per cent. and the sulphur 0.08 per cent. higher.

It is possible that the higher sulphur is due to a little ovomucoid carried down with the coagulum, but this is hardly probable, as the ovalbumin coagulated in the filtrates from these preparations contained 1.61 per cent. of sulphur, which is exactly the quantity found in the most thoroughly purified preparations of ovalbumin.

*Temperature of Coagulation.*—When a solution of conalbumin is heated sufficiently, a finely divided flocculent coagulum separates which is very different from the dense masses that form in a similar solution of ovalbumin. As we could not separate the conalbumin from the other associated proteids except by coagulation, the temperature of coagulation of this albumin could not be determined under definite conditions. The temperature at which this substance begins to coagulate is influenced by the proportion of salts present. From a solution containing 10 per cent. of sodium chloride it separates at a lower temperature than from solutions in pure water. From the former solutions it apparently separated completely below 60°, whereas from the latter it is impossible to separate it from the ovalbumin because the latter begins to coagulate before the separation of the conalbumin is complete.

From solutions containing 10 per cent. of sodium chloride the preparations D.3.1 and K.3.1 separated below 60°, the solutions becoming turbid at about 55°. When 2.5 per cent. of K.3, D.3, and F.3 were each dissolved in 10 per cent. brine their solutions became turbid at 57°, 52°, and 58°, and flocks separated at 58°, 55°, and 59°, respectively.

*Specific Rotation.*—This we were unable to determine directly but indirectly the following results were obtained: of F.1, 1.5 grams were dissolved in 10 per cent. brine, the solution heated to 65°, and the coagulum filtered out and washed. The filtrate was heated to 98° and the coagulum also filtered out and washed. The nitrogen was then determined in each coagulum and in the final filtrate, and the proportion of conalbumin, calculated on the dry preparation, was found to be 25 per cent; of ovalbumin

62.7 per cent; and of ovomucoid 12.2 per cent. Subtracting the amount of rotation due to the sums of the two latter from the total rotation of F.1, we found the amount of rotation caused by the 25 per cent. of conalbumin, which for 100 per cent. was equal to  $[\alpha]_D - 39^\circ$ .

In the same way we found F.3 to contain 36.6 per cent. of conalbumin, 39.7 per cent. of ovalbumin, and 23.7 per cent. of ovomucoid, from which we calculated for the conalbumin  $[\alpha]_D - 36^\circ$ . F.2.a contained 30.9 per cent. conalbumin, 48.9 per cent. ovalbumin, and 20.4 per cent. ovomucoid, so that in this preparation we found  $[\alpha]_D$  equal to  $-36^\circ 21'$ .

Of course such determinations cannot be accepted as final but they are sufficiently accurate to show that conalbumin has a different specific rotation from ovalbumin and is therefore a different substance. This conalbumin appears to be identical with albumin II, described by Panormoff,<sup>1</sup> but so far as we can infer from this abstract of his original paper<sup>2</sup> the substance which he describes under this designation corresponds very closely with our fractions C.3, D.1, D.2, and D.3, whose mean rotation and other properties are the same as those given for albumin II.

These fractions we have shown to be mixtures of ovalbumin, conalbumin, and ovomucoid.

*Ovomucoid.*—After separating all the proteids coagulable by heat, Neumeister<sup>3</sup> found in the white of eggs a substance which he called pseudopeptone. Later Mörner<sup>4</sup> showed this to be a glycoproteid and named it ovomucoid, under which name it is now generally known.

In Table I it is to be noticed that all the fractions following those of the crystallized ovalbumin show an increasing value for  $[\alpha]_D$  and proportional thereto an increasingly greater content of sulphur. This is chiefly due to ovomucoid associated with these fractions. In connection with the detection of sugar in the albumin molecule, it is important to recognize the difficulty with which ovomucoid can be separated from ovalbumin by fractional precipitation with ammonium sulphate.

As we have just shown, fraction F.1 contained 12.2 per cent.,

<sup>1</sup> *Chem. Centrbl.*, 11, 487 (1898).

<sup>2</sup> *Jour. russ. phys. chem. Ges.*, 30, 302.

<sup>3</sup> *Ztschr. Biol., N. F.*, 9, 369 (1890).

<sup>4</sup> *Ztschr. physiol. Chem.*, 18, 525 (1893).

F.3, 23.7 per cent., and F.2.a, 20.4 per cent. of ovomucoid. These fractions were obtained from those immediately following the separation of the crystalline ovalbumin, and F.1 was precipitated by simply adding an equal volume of saturated ammonium sulphate solution to the solution of these fractions.

We have obtained two preparations of ovomucoid in sufficient quantity for analysis and have found them, when dried at  $110^{\circ}$ , to have the following composition, which agrees with that given by Zanetti<sup>1</sup> and by Mörner<sup>2</sup>.

## COMPOSITION OF OVOMUCOID.

	E.4	D.3.3.	Zanetti. <sup>1</sup>		Mörner. <sup>2</sup>
Carbon .....	49.02	48.90	48.94	48.75	....
Hydrogen .....	6.45	6.61	6.94	6.90	....
Nitrogen .....	12.71	22.16	12.46	....	12.65
Sulphur .....	2.38	2.34	2.22	....	2.20
Oxygen .....	29.44	29.99	29.44	....	....
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00		

The specific rotation was found to be E.4,  $-61^{\circ} 38'$ ; D.3.3,  $-61^{\circ} 10'$ ; F.3.3,  $-61^{\circ} 20'$ ; K.3.3,  $-61^{\circ} 30'$ .

## NOTE.

*The Employment of Ammonium Molybdate as a Test for Tin.*—In the April number of this Journal there is a note by Mr. Allen Rogers on the use of ammonium molybdate as “a very delicate test for tin.” Mr. Rogers does not refer to my paper on this subject in the *Chemical News* for December 15 last,<sup>3</sup> and I shall therefore assume that he has not seen it. Perhaps I may therefore be permitted to state briefly the substance of that paper.

Although the color reaction involved is a well-known test for molybdenum, I have been unable to find that, prior to the appearance of my paper, it had ever been suggested as a test for tin; and, having regard to its extreme delicacy in this respect, it seems highly improbable if it had been, that the fact would have been allowed to go into oblivion. My own experience, and I

<sup>1</sup> *Ann. di Chim. e Farmac.*, No. 12, 1897.

<sup>2</sup> *Zeit. physiol. Chem.*, 18, 525.

<sup>3</sup> *Chem. News*, 79, 282 (1899).



believe that of others also, is that the detection of tin in complex mixtures is, with the methods of the text-books, a great difficulty to students, whereas the test now proposed makes it exceedingly easy—assuming ordinary care to be taken.

For the success of this method, two important points must be attended to: *First*, in reducing stannic chloride to stannous chloride, the zinc employed must be entirely free from traces of tin. Samples of commercial zinc that I tried were found quite useless for the purpose. I employed pure zinc supplied by Harrington's for my experiments. *Second*, since a very dilute stannous solution, on exposure to air, becomes oxidized to stannic in a marvelously short time, as soon as the zinc and tin are completely dissolved in hydrochloric acid and the solution is diluted, the ammonium molybdate must be added at once.

I observe that Mr. Rogers finds that "a solution of stannic chloride containing 0.0000042 gram to 1 cc. gives a faint blue color with ammonium molybdate." This corresponds to 1 part of stannous chloride in rather less than 240,000 parts of solution. Had he used boiled water in making up his solution, he would have found that the delicacy of the test is far greater than this. By taking the precautions described in my paper, I was enabled to get a delicacy of 1 in 1,500,000. I concluded, however, that under ordinary conditions of working, a very distinct blue color is given by the presence of 1 part of stannous chloride in anything up to 100,000 parts of solution.

I am very glad to find that Mr. Rogers confirms my experience in three points: (1) that ammonium molybdate is a much better reagent than mercuric chloride for stannous chloride; (2) that the reagent must not be added without first of all diluting the hydrochloric acid present in the solution to be examined; and (3) that the ordinary laboratory reagent gives results that are most satisfactory.

I shall merely add that the method has been used in this laboratory during the past five months with uniform success.

J. P. LONGSTAFF.

CHEMICAL LABORATORY, UNIVERSITY OF EDINBURGH, May 22, 1900.

## NEW BOOKS.

**RÉPERTOIRE GÉNÉRAL OU DICTIONNAIRE METHODIQUE DE BIBLIOGRAPHIE DES INDUSTRIES TINCTORIALES ET DES INDUSTRIES ANNEXES DEPUIS LES ORIGINES IUSQU' A LA FIN DE L'ANNEE, 1896. Technologie et Chimie. Par Jules Garçon. Tome I. Paris: Gauthier-Villars. 1900. 74 pp. Premier Fascicule.**

This dictionary of the bibliography of the dyeing industries and allied subjects, is one of the most important pieces of bibliographical work that has ever been attempted for the use and convenience of chemists and technologists. It originated with the chemical section of the Société Industrielle de Mulhouse in 1892, and, after a labor of five years, the finished work was submitted to the society in 1897, when, after careful examination at the hands of a commission of experts, it was awarded the Daniel Dollfus grand prize of 5,000 francs and a medal of honor. The magnitude of this piece of bibliography will be understood when we state that the author makes reference to some 2,000 distinct works and to 110 periodicals, which latter make up about 5,000 volumes more. The first part of Vol. I, at present under notice, is devoted to the introduction, outlining the scope of the work and giving a list of the bibliographic sources availed of, both official publications and records and general and special bibliographical publications and catalogues; an alphabetical list of subject-headings under which the material is arranged; and a list of the periodicals from which the references are taken. The second part of Vol. I will be devoted to the indices of authors cited and subjects treated, while Vols. II and III will be the reference dictionary proper arranged under the various subject-headings. The scheme seems, on examination, to be a very complete one and the part of the work now in hand promises well for the way in which it will be executed.

The first part of Volume I has been issued, as just noticed, and the second part of the volume is stated to be now in press; Volume II is ready for distribution and Volume III is promised by the end of 1900.

S. P. SADTLER.

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## THE CHEMISTRY OF CORN OIL.

BY HERMANN T. VOLTE AND HARRIET WINFIELD GIBSON.

Received May 7, 1900.

### DETERMINATION OF THE CONSTANTS.

THE samples of corn oil, the determination of whose constants has been reported in the present article, are here designated as Nos. I, II, and III.

*Oil No. I* is a commercial article, bought of a reputable dealer and intended for use in the manufacture of cheap paints. It has been kept in a corked tin can for six to seven years. It is of a bright, golden yellow color, is free from foots, and has a pronounced grain-like odor.

*Oil No. II* is a sample freshly prepared by hydraulic pressure and is of undoubted purity. Its color is somewhat lighter and its grain-like odor more marked than that of oil No. I.

*Oil No. III* is a product of the mash of distilleries. It is golden brown in color and from ten to twelve years old. The properties of this oil have been so affected by the process of manufacture that it is practically distinct from the other samples examined. For this reason and because this method of manufacture is now obsolete, its examination was dropped at an early stage.

DETERMINATION OF PHYSICAL CONSTANTS.

A. *Specific Gravity.*

the Sprengel tube and the Westphal balance were used in this determination, although but little reliance can be placed on the latter beyond the second place of decimals.

*Results Obtained:*

OIL No. I.					
	Wt. water 15.5° C. Grams.	Wt. oil 15.5° C. Grams.	Wt. oil at 100° C. Grams.	Sp. gr. 15.5° C.	Sp. gr. 100° C.
.....	1.5265	1.4068	1.3315	0.9216	0.8722
.....	1.6404	1.5113	1.4297	0.9213	0.8715
.....	1.3602	1.2528	1.1848	0.9210	0.8710
Average for Sprengel tube.....				0.9213	0.8716
Westphal balance.....				0.921	0.895

OIL No. II.					
.....	2.0130	1.8547	1.7554	0.92136	0.87203
.....	2.1788	2.0072	1.8958	0.92124	0.87011
Average for Sprengel tube.....				0.9213	0.87107
Westphal balance.....				0.921	.....

OIL No. III. <sup>1</sup>					
.....	1.0037	0.9288	0.8789	0.9253	0.8746
.....	1.5718	1.4551	1.3780	0.9257	0.8767
Average for Sprengel tube.....				0.9255	0.8756
Westphal balance.....				0.9255	.....

*Comparison with Results of Other Observers.*

°C.	Observer.	Reference.
60	Rokitianski <sup>2</sup>	<i>Ph. Russ.</i> (1894), 712-713.
60	Curtmann	<i>Chem. Centrbl.</i> , 59, 1193.
70	Bowers <sup>2</sup>	<i>Pharm. J.</i> , Nov., 1889.
100	Shuttleworth	<i>Pharm. J.</i> , 16, 1095.
15	Schaedler	<i>J. Soc. Chem. Ind.</i> , 11, 504.
16	Procter	<i>J. Soc. Chem. Ind.</i> , 17, 11.
15-0.9244	De Negri and Fabris	<i>Ztschr. anal. Chem.</i> , 33, 547-71.
20	Trimble	<i>Am. J. Pharm.</i> , 58, 265.
39	Hart <sup>2</sup>	<i>Chem. Ztg.</i> , 17, 1522.
38-0.9262	Hopkins	<i>This Journal</i> , Dec., 1898.
43	Dulière	<i>J. Pharm.</i> (1897), 217.
44	Smith	<i>J. Soc. Chem. Ind.</i> , 11, 504-5.
45	DeNegri <sup>2</sup>	<i>Chem. Ztg.</i> , 22, 961-976.
62	Mills	<i>J. Soc. Chem. Ind.</i> , 11, 504-5.

<sup>1</sup> Ten-year-old sample of oil from mash of distillery.

<sup>2</sup> Petroleum ether extract.

<sup>3</sup> Dark brown oil.

B. Viscosity.

This determination was made by means of a Boverton-Redwood viscosimeter and the instrument standardized for both distilled water and rape oil at 20° C.

Results Obtained:

	Tempera- ture.	Av. time of flow. Seconds.	Viscos. water.	Viscos. water.
Distilled water.....	20°	29	1.00	.....
Rape oil.....	20°	405.5	....	100.00
Oil No. I.....	20°	283.7	9.79	70.42
Oil No. II.....	20°	297.7	10.27	73.89

Comparison with Results of Other Observers:

Tempera- ture.	Viscos. water.	Viscos. rape.	Observer.	Reference.
18° C.-19° C	....	61.1	Smith	<i>J. Soc. Chem. Ind.</i> , 11, 504.
15° C.	19.2	...	Andés	"Veg. Fats and Oils."
Viscosity of almond oil			Shuttleworth	<i>Pharm. J.</i> , 16, 1095.
Viscosity greater than olive			Bowers	<i>Pharm. J.</i> , Nov., 1889.

C. Index of Refraction.

The instrument used for this determination was Abbé's refractometer.

Results Obtained:

OIL No. I. —			
	Temperature.	A.	T.
1 .....	15° C.	1.4768	35.8
2 .....	15° C.	1.4766	36.0
3 .....	20° C.	1.4762	35.9
4 .....	20° C.	1.4760	35.9
Average for .....	15° C.	1.4767	35.9
Average for .....	20° C.	1.4761	35.9
OIL No. II.			
1 .....	15° C.	1.4765	35.8
2 .....	15° C.	1.4766	36.0
3 .....	15° C.	1.4767	36.0
Average for .....	15° C.	1.4766	35.9
OIL No. III.			
1.....	19.5° C.	1.4767	36.2
2.....	20° C.	1.4766	36.2
3.....	20.5° C.	1.4764	36.3
Average for.....	20° C.	1.4765	36.2

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*Comparison with Results of Other Observers :*

Temperature.	Refractive index.	Observer.	Reference.
20° C.	1.4765	Proctor	<i>J. Soc. Chem. Ind.</i> , 17, 11.

DETERMINATION OF CHEMICAL CONSTANTS—QUANTITATIVE.

*A. Free Acid.*

The method given in Allen's "Commercial Organic Analysis" (I), 104, was used in this determination, substituting a mixture of 9 parts neutral alcohol and 1 part ether for the distilled spirit. The percentage of free acid was calculated from the acid.

*Results Obtained :*

OIL No. I.					
	Wt. oil. Grams.	Vol. N/10 KOH. cc.	Acid value.	Free acid. Per cent.	Degrees acidity.
.....	10.6617	7.0	3.68	1.851	6.56
.....	7.2552	4.8	3.71	1.851	6.62
Average.....			3.70	1.851	6.59
OIL No. II.					
.....	9.9294	4.0	2.26	1.136	4.03
.....	13.0816	5.2	2.23	1.121	3.97
Average.....			2.25	1.128	4.00
OIL No. III.					
.....	4.2351	15.6	20.64	10.387	36.83
.....	6.2726	23.1	20.66	10.385	36.83
Average.....			20.65	10.386	36.83

*Comparison with Results of Other Observers :*

Free acid, per cent.	Observer	Reference.
0.75	Hart	<i>Chem. Ztg.</i> , 17, 1522.
0.88	Lloyd	<i>Chem. Centrbl.</i> , 59, 257.
0.00	Spüller	<i>Ding. poly. J.</i> , 264, 626.
5.65	De Negri	<i>Chem. Ztg.</i> , 22, 961-976.

*B. Iodine Absorption Hübl Figure.*

*Necessary Solutions.—*

IgCl<sub>2</sub> in 95 per cent. alcohol, 60 grams per liter.

Iodine in 95 per cent. alcohol, 50 grams per liter.

The alcohol used was purified by oxidation with potassium permanganate and subsequent distillation over calcium carbonate. The distillate was rejected until no discoloration was

shown on heating a small portion with a lump of solid potash for ten minutes.

3. N/10 sodium thiosulphate.

4. Twenty per cent. solution of potassium iodide in distilled water.

5. Solution of boiled starch as indicator.

*Process.*—Thin Erlenmeyer flasks, having accurately fitted ground-glass stoppers and flaring mouths, thus forming a gutter between flask and stopper, were used for this operation.

Equal parts of solutions 1 and 2 were mixed twenty-four hours before each test and allowed to stand in the dark until needed. About 0.250 gram oil was weighed into a test flask, the oil dissolved in 10 cc. chloroform, and 25 cc. of the mixed Hübl solution added. The excess of Hübl solution was afterward found to be about 100 per cent. The flask was then stoppered, the gutter filled with potassium iodide solution, and the whole set away in the dark for twenty-four hours. A blank was run for every determination.

After twenty-four hours the stopper was removed, sufficient potassium iodide solution added to the contents of the flask to prevent any precipitation of mercuric iodide and enough distilled water to make the bulk convenient for titration. The liquid was then titrated with N/10 sodium thiosulphate, starch indicator.

*Results Obtained:*

OIL No. I.

	Wt. oil. Gram.	Vol. hypo. cc.	Wt. iodine. Gram.	Iodine absorption. Per cent.
1.....	0.1986	18.9	0.235323	118.44
2.....	0.2466	23.7	0.295088	119.66
3.....	0.2677	26.0	0.323725	120.90
4.....	0.22835	22.0	0.273921	119.95
Average Hübl figure.....				119.74

OIL No. II.

	Wt. oil. Gram.	Vol. hypo. cc.	Wt. iodine. Gram.	Iodine absorption. Per cent.
1.....	0.2708	26.2	0.322183	118.97
2.....	0.2441	23.3	0.290108	118.85
3.....	0.2697	25.7	0.319990	118.65
4.....	0.3070	29.1	0.326232	118.02
Average Hübl figure.....				118.62

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OIL No. III.				
	Wt. oil. Gram.	Vol. hypo. cc.	Wt. iodine. Gram.	Iodine absorption. Per cent.
.....	0.2199	20.1	0.250264	113.80
.....	0.2894	26.2	0.326215	112.72
.....	0.2559	23.4	0.291352	113.85
.....	0.2453	22.2	0.276471	112.70
Average Hübl figure.....				113.27

*Comparison with Results of Other Observers :*

figure.	Observer.	Reference.
	Rokitianski	<i>Ph. Russ.</i> (1894), 712-713.
-123	De Negri and Fabris	<i>Ztschr. anal. Chem.</i> , 33, 547-72.
7	De Negri	<i>Chem. Ztg.</i> , 22, 961-976.
	Smetham	<i>Analyst</i> , 18, 191-193.
	Hart	<i>Chem. Ztg.</i> , 17, 1522.
	Hazura	<i>Ztschr. angew. Chem.</i> (1888), 696.
-119.9	Spüller	<i>Ding. poly. J.</i> , 264, 626.
-122.7	Lane	<i>J. Chem. Soc.</i> (1893), A, 153.
	Hehner	<i>J. Soc. Chem. Ind.</i> , 16, 87.
	Wallenstein	<i>Chem. Ztg.</i> (1894), 18, (ii), 119.
-123.1	Hopkins	<i>This Journal</i> , Dec., 1898.
5	Dulière	<i>J. Pharm.</i> (1897), 217.
	Mills	<i>J. Soc. Chem. Ind.</i> , 11, 504.

*C. Saponification Value (Koettstorfer Figure).*

method here employed was that given in Allen's "Com-  
l Organic Analysis," II (I), 56-57. The alcohol em-  
was prepared as described under "Iodine Values," and  
k run side by side with the test for each determination.

*Results Obtained :*

OIL No. I.					
	Wt. oil. Grams.	Vol. N/HCl. cc.	Koettstorfer fig.	Sapon. equiv.	Ether value.
.....	2.0127	6.95	193.71	289.61	190.01
.....	2.5187	8.60	191.55	292.88	187.85
.....	2.4600	8.45	192.70	291.13	189.00
verage .....			192.65	291.21	188.95

OIL No. II.					
.....	3.8356	13.20	193.07	290.57	190.82
.....	5.2317	18.05	193.55	289.85	191.30
.....	2.5611	8.75	191.31	293.24	189.06
verage .....			192.64	291.22	190.39

OIL No. III.					
.....	1.9700	6.75	190.29	294.81	169.64
.....	2.2206	7.65	193.26	290.28	172.61
verage .....			191.78	292.55	171.13



*Comparison with Results of Other Observers :*

Koettstorfer fig.	Sapon. equiv.	Observer.	Reference.
182.81	306.9	De Negri	<i>Chem. Ztg.</i> , 22, 961-976.
188.1-189.2	298.3-296.6	Spüller	<i>Ding. poly. J.</i> , 264, 626.
188-193	298.4-290.7	De Negri and Fabris	<i>Ztschr. anal. Chem.</i> , 33, 547.
189.5	296	Hart	<i>Chem. Ztg.</i> , 17, 1522.
193.4	290.07	Mills	<i>J. Soc. Chem. Ind.</i> , 11, 504.
198.5	282.6	Smetham	<i>Anal.</i> , 18, 191-193.
198.8-203	282.2-276.4	Dulière	<i>J. Pharm.</i> (1897), 217.

*D. Insoluble Fatty Acids (Hehner Figure).*

From 2 to 4 grams of oil were dissolved in ether in a beaker. Fifty cc. of alcoholic potash (made by dissolving about 20 grams potassium hydroxide in 500 cc. purified and redistilled 95 per cent. alcohol) were added to the ethereal solution and the whole heated on a water-bath until saponification was effected. The liquid was then diluted with hot distilled water and heated until the ether and alcohol were entirely expelled. The aqueous soap solution thus formed was broken up with dilute hydrochloric acid and heating continued until the insoluble fatty acids formed a clear oily layer.

The fatty acids were then washed with boiling distilled water until the filtrate was neutral to methyl orange. An unusual amount of washing was found necessary with this oil, owing to the large proportion of an acid difficultly soluble in hot water. About 1500 cc. of wash-water were used and, as will be seen by the results, the amount of insoluble acids found to be unusually low.

*Results Obtained :*

## OIL No. I.

	Wt. oil taken. Grams.	Wt. insol. fatty acids. Grams.	Hehner value.
1.....	4.6700	4.3256	92.63
2.....	2.6092	2.4121	92.45
3.....	2.3161	2.1609	93.29
Average Hehner value.....			92.79

## OIL No. II.

	Wt. oil taken. Grams.	Wt. insol. fatty acids. Grams.	Hehner value.
1.....	3.5853	3.2678	91.14
2.....	3.2331	3.0142	93.23
3.....	2.6079	2.4079	92.33
Average Hehner value.....			92.23

## OIL No. III.

	Wt. oil taken. Grams.	Wt. insol. fatty acids. Grams.	Hehner value.
1.....	3.9832	3.5102	88.12
2.....	2.8297	2.4995	88.30
Average Hehner value.....			88.21

*Comparison with Results of Other Observers:*

Hehner value.	Observer.	Reference.
93.40	Hoppe-Seyler .	<i>Bull. Soc. Chim.</i> (1866), [2], 6, 342.
93.57	Hopkins	This Journal, Dec., 1898.
94.70	Spüller	<i>Ding. poly. J.</i> , 264, 626.
95.70	Hart	<i>Chem. Ztg.</i> , 17, 1522.
96.70	Lloyd	<i>Chem. Centrbl.</i> , 59, 1193.

*E. Volatile Acids (Reichert Figure).*

Precisely 2.5 grams oil were saponified as in the Koettstorfer process, evaporating off the alcohol completely. Fifty cc. distilled water, containing 1 cc. phenolphthalein indicator, were then added to the dried soap and the whole heated on the water-bath until the soap was completely dissolved. While still warm the aqueous soap solution was titrated with N/2 sulphuric acid, overrunning 2 cc. The total volume of liquid was now 60–65 cc. The decomposed soap solution was then slowly distilled into a similar flask, containing 50 cc of N/10 potassium hydroxide and 1 cc. phenolphthalein indicator. A large percentage of a solid fatty acid also distilled over in white flakes, but was held back by a small wetted filter, placed in the neck of the receiving flask.

When about 50 cc of the liquid in the distilling flask had gone over, 50 cc. of distilled water were added to the residue and the distillation repeated. The contents of the receiver were then titrated back with N/10 hydrochloric acid and the "Reichert figure" calculated from the amount of volatile acids thus recovered from the two distillations.

*Results Obtained:*

## OIL No. I.

	Vol. N/10 HCl.	Reichert figure.	Wt. KOH for 100 g. oil. Gram.
1 .....	45.8	4.2	0.94248
2 .....	45.6	4.4	0.98736
Average.....			4.3
			0.96492

## OIL No. II.

1 .....	46.0	4.0	0.89760
2 .....	45.6	4.4	0.98736
Average.....			4.2
			0.94248

## OIL No. III.

	Vol. N/10 HCl.	Reichert figure.	Wt. KOH for 100 g. oil. Grams.
1 .....	39.9	10.1	2.26644
2 .....	40.3	9.7	2.17668
Average.....		9.9	2.22156

*Comparison with Results of Other Observers :*

Reichert value.	Observer.	Reference.
0.33	Spüller	Ding. <i>poly. J.</i> , 264, 626.
2.5 <sup>1</sup>	Smith	<i>J. Soc. Chem. Ind.</i> , 11, 504.
6.7 <sup>2</sup>	Morse	<i>N. H. Expt. Sta. Bull.</i> (1892), 16, 19.
0.0	Hopkins	This Journal, Dec., 1898.

*F. Acetyl Value.*

The method used was that given in Allen's "Commercial Organic Analysis," II (I), 64-65, the "Filtration Process" being the one employed.

*Results Obtained :*

## OIL No. I.

	Wt. oil. Grams.	Vol. N/HCl. cc.	Koettstorfer fig.	Vol. N/10 KOH. cc.	Acetyl value.
1 .....	2.3420	8.8	210.8	4.5	10.78
2 .....	2.0092	7.6	212.2	4.1	11.45
Average .....			211.5	..	11.12

## OIL No. II.

1 .....	1.8641	7.1	213.7	3.7	11.14
2 .....	1.4686	5.5	210.1	3.1	11.84
Average .....			211.9	..	11.49

*Comparison with Results of Other Observers :*

Koetts- torfer fig.	Acetyl value (filtr.).	Observer.	Reference.
201.5	8.25	Lewkowitsch	Allen's "Com. Org. Anal.," Vol. II, 68.
200.9	7.90	Lewkowitsch	Allen's "Com. Org. Anal.," Vol. II, 68.

*G. Glycerol.*

Hehner's dichromate method, as given in Allen's "Commercial Organic Analysis," II (I), 316-317, was employed for this determination.

*Results Obtained :*

## OIL No. I.

	Wt. oil. Grams.	Vol. K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> . cc.	Wt. glycerol. Grams.	Glycerol. Per cent.
1 .....	2.6092	27.57	0.276395	10.59
2 .....	2.3361	24.46	0.245217	10.50
Average .....				10.545

<sup>1</sup> Calculated. . 100 parts oil require 0.56 part KOH.

<sup>2</sup> Calculated. Reported as 3.2 per cent. volatile acids.

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	OIL No. II.			
	Wt. oil. Grams.	Vol. $K_2Cr_2O_7$ . cc.	Wt. glycerol. Grams.	Glycerol Per cent.
1.....	2.5701	26.37	0.264359	10.29
2.....	2.0425	21.21	0.212635	10.41
Average .....				10.35

*H. Phytosterol.*

The process of Foster and Reichelmann, as given in the *Analyst* (97), 131, was employed in this determination. The crude phytosterol, resulting from the evaporation of the ethereal extract, was estimated as unsaponifiable matter.

*Results Obtained:*

	Wt. oil. Grams.	Wt. ether residue. Gram.	Unsap. matter Per cent.
Oil No. I.....	55.3945	0.7691	1.39
Oil No. II .....	49.1123	0.7036	1.43
Average .....			1.41

*Comparison with Results of Other Observers:*

Unsap. matter. Per cent.	Observer.	Reference.
1.35	Spüller	Ding. poly. J., 264, 626.
1.55	Hart	Chem. Ztg., 17, 1522.
2.86	Hopkins	This Journal, Dec., 1898.

DETERMINATION OF CHEMICAL CONSTANTS—MISCELLANEOUS.

*A. Color Reactions with Sulphuric Acid.*

*Heidenreich's Test.*—Two drops concentrated sulphuric acid were allowed to fall into the center of 20 drops of oil on a watch-glass. The oil and acid were then stirred together with a glass

rod. Before stirring, all three oils gave a rayed ring of mahogany on golden brown background.

After stirring, oils I and II gave a dark red-brown, while oil III gave a dull claret, all of honey-like consistency.

*I. Carbon Disulphide Test.*—One drop concentrated sulphuric acid was added to a solution of a few drops of oil in carbon disulphide; the mixture was well shaken and allowed to stand. All three oils gave a fine violet after twenty-four hours.

*B. Color Reactions with Nitric Acid.*

*Hauchecorne's Test.*—From 3 to 5 parts oil by volume were shaken with 1 part nitric acid (sp. gr. 1.32). The mixture was then

heated on the water-bath for five minutes and allowed to stand.

Oils I and II gave an orange-yellow oily layer of consistency of thick honey.

Oil III gave a mahogany-red layer of much less viscosity.

*II. Massie's Test.*—Three parts oil by volume were shaken with 1 part nitric acid (sp. gr. 1.42) for two minutes and allowed to stand.

Oils I and II gave a bright mahogany-red oily layer of great viscosity.

Oil III gave a dark, reddish brown layer of less viscosity.

*Comparison with Results of Other Observers :*

HNO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Observer.	Reference.
Yellow-orange	.....	Dulière	<i>J. Pharm.</i> (1897), 217.
.....	Dark red	Hart	<i>Chem. Ztg.</i> , 17, 1522.
Reddish (Massie)	Black-brown	Shuttleworth	<i>Pharm. J.</i> , 16, 1095.
Reddish yellow	Green	Brannt	"An. and Veg. Fats and Oils."

*C. Silver Nitrate Reduction Tests.*

*I. Becchi's Test—Process of Pearmain and Moor.*—Ten cc. of oil were shaken with 2 cc. of a reagent prepared by dissolving 1 gram silver nitrate in 100 cc. 95 per cent. alcohol, then adding 20 cc. ether and 1 drop of nitric acid. The mixture was then placed in boiling water for ten minutes.

All three oils gave a dark brown coloration.

*II. Brullé's Test.*—Twelve cc. of oil were shaken with 5 cc. of a solution prepared by dissolving 2.5 grams silver nitrate in 100 cc. of 95 per cent. alcohol. The mixture was then heated in boiling water twenty minutes.

All three oils were colored intensely black.

*Comparison with Results of Other Observers :*

Becchi.	Brullé.	Observer.	Reference.
Slightly darkened	.....	Hart	<i>Chem. Ztg.</i> , 17, 1522.
Faint brown	Black	De Negri	<i>Chem. Ztg.</i> , 22, 961-976.

*D. Elaidin Reaction (Poutet's Method).*

One cc. of mercury was dissolved in 12 cc. of cold nitric acid (sp. gr. 1.42); 2 cc. of the freshly prepared green solution were added to 50 cc. of oil contained in a wide-mouthed, stoppered bottle, the contents of the bottle violently shaken and the agitation

repeated every ten minutes for two hours. The oil was then allowed to stand undisturbed in a warm room.

*Results Obtained.*—All three oils.

After two hours, orange-yellow deposit, pasty in consistency and small in amount. Orange-red, viscous liquid above.

After two weeks, little change except in gradual darkening of color and decrease in viscosity of supernatant liquid.

*Comparison with Results of Other Observers:*

Result of test.	Observer.	Reference.
Pasty or buttery mass	Smith	<i>J. Soc. Chem. Ind.</i> , 11, 504.
Orange-yellow color; partial solidification.	Shuttleworth	<i>Pharm. J.</i> , 16, 1095.
Orange-yellow; no solidification.	Dulière	<i>J. Pharm.</i> (1897), 217.
Much olein; between olive and cotton-seed oils.	Lloyd	<i>Chem. Centrbl.</i> , 59, 1193.

*E. Rise in Temperature with Sulphuric Acid.*

In making this determination, Archbutt's method for the Maumené, test, as given in Allen's "Commercial Organic Analysis," II (I), 76–77, was employed. The sulphuric acid used was of 1.842 sp. gr.

*Results Obtained:*

	Initial temp.	Av. rise in temp.	Specific temp.
Distilled water.....	23° C.	42° C.	100
Oil No. I.....	23° C.	75° C.	178.6
Oil No. II.....	23° C.	74° C.	176.2

*Comparison with Results of Other Observers:*

Maumené figure.	Observer.	Reference.
56° C.	Spüller	<i>Ding. poly. J.</i> , 264, 626.
60.5° C.	Hart	<i>Chem. Ztg.</i> , 17, 1522.
79° C.	Jean <sup>1</sup>	<i>J. Soc. Chem. Ind.</i> , 11, 504.
84° C.–89° C.	De Negri and Fabris <sup>2</sup>	<i>Ztschr. anal. Chem.</i> , 33, 547–72.
89° C.	Mills <sup>2</sup>	<i>J. Soc. Chem. Ind.</i> , 11, 504–5.

*F. Heat of Bromination.*

The process of Hehner and Mitchell, as given in Allen's "Commercial Organic Analysis," II (I), 80, was followed in making this determination. Six readings were taken for each sample. The calculated iodine value was found by multiplying the bromine thermal value by 5.5.

<sup>1</sup> Obtained by use of Jean's thermelaeometer.

<sup>2</sup> 15 grams oil + 5 cc. H<sub>2</sub>SO<sub>4</sub>.

*Results Obtained:*

	Br. Therm. Val.	Hübl No.	Calc. I. No.
Oil No. I .....	21.9° C.	119.74	120.45
Oil No. II .....	21.8° C.	118.62	119.90

*Comparison with Results of Other Observers:*

Br. Therm. Val.	Calc. I. No.	Observer.	Reference.
21.5	118.25	Hehner	<i>J. Soc. Chem. Ind.</i> , 16, 87.

*G. Solubility in Glacial Acetic Acid (Valenta's Test).*

In this determination the method of Allen's "Commercial Organic Analysis," II (I), 40, was followed. Three cc. of oil and of acid were employed.

*Results Obtained:*

Oil No. I.—74° C., average of six tests.  
 Oil No. II.—80° C., average of five tests.  
 Oil No. III.—44° C., average of five tests.

*Comparison with Results of Other Observers:*

Turbidity temp.	Observer.	Reference.
65° C.	De Negri <sup>1</sup>	<i>Chem. Ztg.</i> , 22, 961-976.

*H. Oxygen Absorption (Livache Test).*

Finely divided lead powder was obtained by precipitating metallic lead from lead acetate by means of zinc, washing the precipitate rapidly with water, alcohol, and ether, in the order named, and drying it in a desiccator.

Approximately 1 gram of lead powder, prepared as above, was spread in a thin layer on a large watch-glass and a few drops of oil added by means of a pipette, care being taken to keep the drops of oil separate. The amount of oil taken was accurately determined and was not allowed to exceed 0.6 gram. The watch-glass was then exposed to light but protected from dust and allowed to remain, at the ordinary temperature, until it ceased to gain in weight. All samples tested were examined at the same time and under the same conditions.

<sup>1</sup> Obtained by the use of Jean's thermelaeometer.

*Results Obtained:*

OIL No. I.			
Wt. oil. Gram.	Total gain. Gram.	Time required. Days.	Gain. Per cent.
0.5193	0.0310	7	5.97

OIL No. II.			
0.3313	0.0172	10	5.19

## SUMMARY.

TABLE OF PHYSICAL CONSTANTS.

		Oil No. II.	Oil No. I.	Oil No. III.	Insol. fat acids
Specific gravity.....	15.5° C.	0.9213	0.9213	0.9255	.....
Specific gravity.....	100° C.	0.8711	0.8716	0.8756	0.8529
Viscosity (water) ....	20° C.	10.57	9.79	.....	.....
Viscosity (rape) ....	20° C.	73.89	70.42	.....	.....
Index of refraction..	15° C.	1.4766	1.4767	.....	.....
Index of refraction..	20° C.	.....	1.4761	1.4765	.....
Melting-point .....	.....	.....	.....	.....	22.4° C.

TABLE OF CHEMICAL CONSTANTS—QUANTITATIVE.

	Oil No. II.	Oil No. I.	Oil No. III.	Insol. fat acids
Per cent. ash .....	.....	0.065	0.0655	.....
Acid value.....	2.25	3.70	20.65	.....
Per cent. free acid .....	1.128	1.851	10.386	.....
Degrees acidity .....	4.00	6.59	36.83	.....
Per cent. iodine absorption..	118.62	119.74	113.27	120.98
Koettstorfer figure .....	192.64	192.65	191.78	199.15
Saponification equivalent....	291.22	291.21	292.55	281.72
Ether value.....	190.39	188.95	171.13	.....
Hehner value.....	92.23	92.79	88.21	.....
Reichert figure.....	4.2	4.3	9.9	.....
Wt. KOH per 100 grams oil..	0.94248 g	0.96492 g	2.22156 g	.....
Koettstorfer of acetic oil.....	211.9	211.5	.....	.....
Acetyl value.....	11.49	11.12	.....	.....
Per cent. glycerol.....	10.35	10.545	.....	.....
Per cent. unsaponifiable matter	1.43	1.39	.....	.....



TABLE OF CHEMICAL CONSTANTS—MISCELLANEOUS.

	Oil No. II.	Oil No. I.	Oil No. III.	Insoluble fat acids.
Heidenreich— $H_2SO_4$	Mahogany-red to dark red-brown		Mahogany to claret	....
Carbon disulphide— $H_2SO_4$	Golden brown; violet after 24 hours.		Claret; violet in 24 hours.	....
Hauchecorne— $HNO_3$	Orange-yellow		Mahogany	....
Massie— $HNO_3$	Mahogany-red		Dark red-brown	....
Becchi— $AgNO_3$	Dark brown		Dark brown	....
Brullé— $AgNO_3$	Black		Black	....
Elaidin test	Orange-yellow deposit; red liquid		Orange solid; dark red liquid	....
Mauméné—Rise in temp.	74° C.	75° C.	.....	....
Mauméné—Specific temp.	176.2	178.6	.....	....
Bromine thermal value	21.8° C.	21.9° C.	.....	21.6° C.
Valenta's test	80° C.	74° C.	65° C.	....
Livache test—Per cent. gain	5.19 in 10 days	5.97 in 7 days.	.....	....

# APPARATUS FOR THE DETERMINATION OF AMMONIA IN WATER, BY THE WANKLYN METHOD, AND TOTAL NITROGEN BY THE KJELDAHL METHOD.

BY ROBERT SPURR WESTON.

Received June 12, 1900.

THE introduction of the ammonia method by Wanklyn<sup>1</sup> in 1867 has been followed by many modifications of the original apparatus. Like modifications have followed the introduction of the method introduced by Kjeldahl<sup>2</sup> in 1883.

Wanklyn originally used a tubulated retort and a Liebig condenser. The copper condenser contained a glass tube 90 cm. long and 3 cm. in diameter, thus allowing the beak of the retort to enter the condenser tube. The joint was made by wrapping a little writing paper around the beak of the retort where it entered the condenser tube. Such an apparatus is friable and unhandy.

This single still has been improved upon by various analysts, until there are several forms in use which satisfy most requirements.

An excellent form is described by Cairns<sup>3</sup> and consists of a 2 liter, glass stoppered flask with a side-neck tube. The tube is bent so as to point vertically downward at a convenient distance from the flask. A copper condenser carrying a block-tin zigzag is attached to the neck of the flask by a rubber tube, and the lower end of the condenser is arched upward to prevent the condensed atmospheric moisture from contaminating the distillate. Leffmann<sup>4</sup> makes use of a tubulated retort with a bent neck, connected with a spiral glass worm.

Perhaps the most durable and, all things considered, most convenient form of single still is the one designed by Dr. A. H. Gill and used for several years by Mrs. E. H. Richards in the laboratory of the Massachusetts Board of Health.

This still consists of a flask holding about 1300 cc., which is closed by a cork carrying a  $\frac{3}{8}$  inch glass tube. This glass tube is bent so as to enter a  $\frac{1}{4}$  inch straight block-tin condenser

<sup>1</sup> Wanklyn: "Water Analysis," 1868.

<sup>2</sup> *Ztschr. anal. Chem.*, 23, 557.

<sup>3</sup> "Quantitative Analysis," New York, 1896, p. 271.

<sup>4</sup> Leffmann: "Examination of Water," Philadelphia, 1895.

tube. The joint between the glass and tin tubes is made with a cork which is bored half way on one side to receive the glass, and half way on the other side to receive the tin tube. A rubber collar is slipped on to the lower end of the condenser tube to prevent the contamination of the distillate. The condenser is perpendicular and the neck of the flask makes an angle of  $45^\circ$  with it.

This apparatus has many advantages. It is easily boiled clean. Breakage of parts is not frequent, and the broken parts themselves can be replaced at a small cost. The inclined flask is also a decided advantage when the contents have a tendency to bump.

When many stills are used at once, however, these single stills are not so convenient. They take up much bench room unnecessarily, and when the condenser tubes are run through a common cooling tank, the distilling and receiving vessels are on opposite sides and are therefore somewhat inconveniently placed. Perhaps the best arrangement in using a common condenser is that described by Mason.<sup>1</sup>

For the determination of nitrogen according to the Kjeldahl method, many forms of still have been introduced. It has been desirable from the beginning, however, to arrange groups of stills. Two forms are in general use.

At the Halle Agricultural Experiment Station an apparatus<sup>2</sup> is used which makes use of an air condenser, but the general arrangement of parts is similar to that used by Mason for water analysis, though Erlenmeyer flasks are used for distilling- and receiving-vessels.

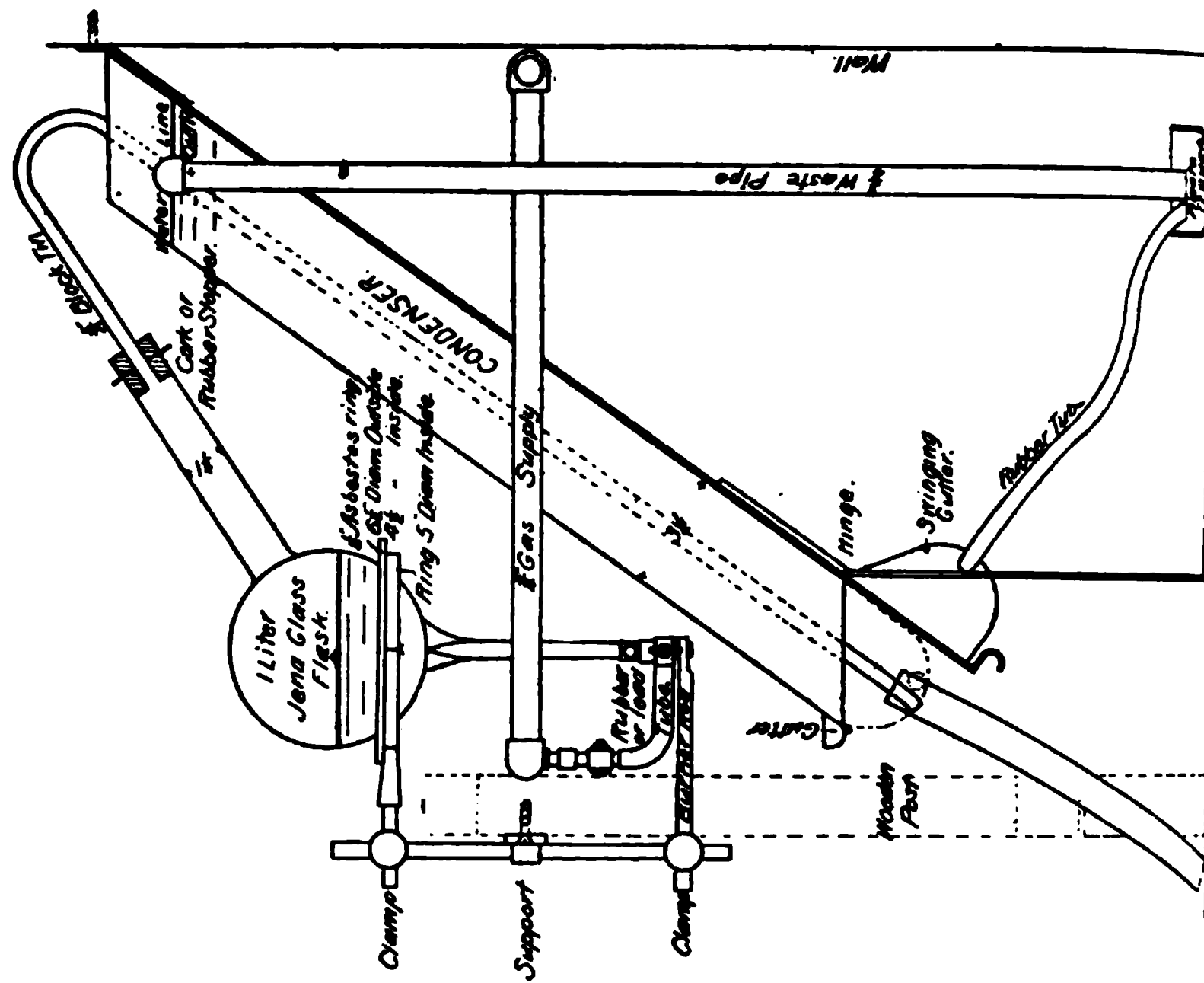
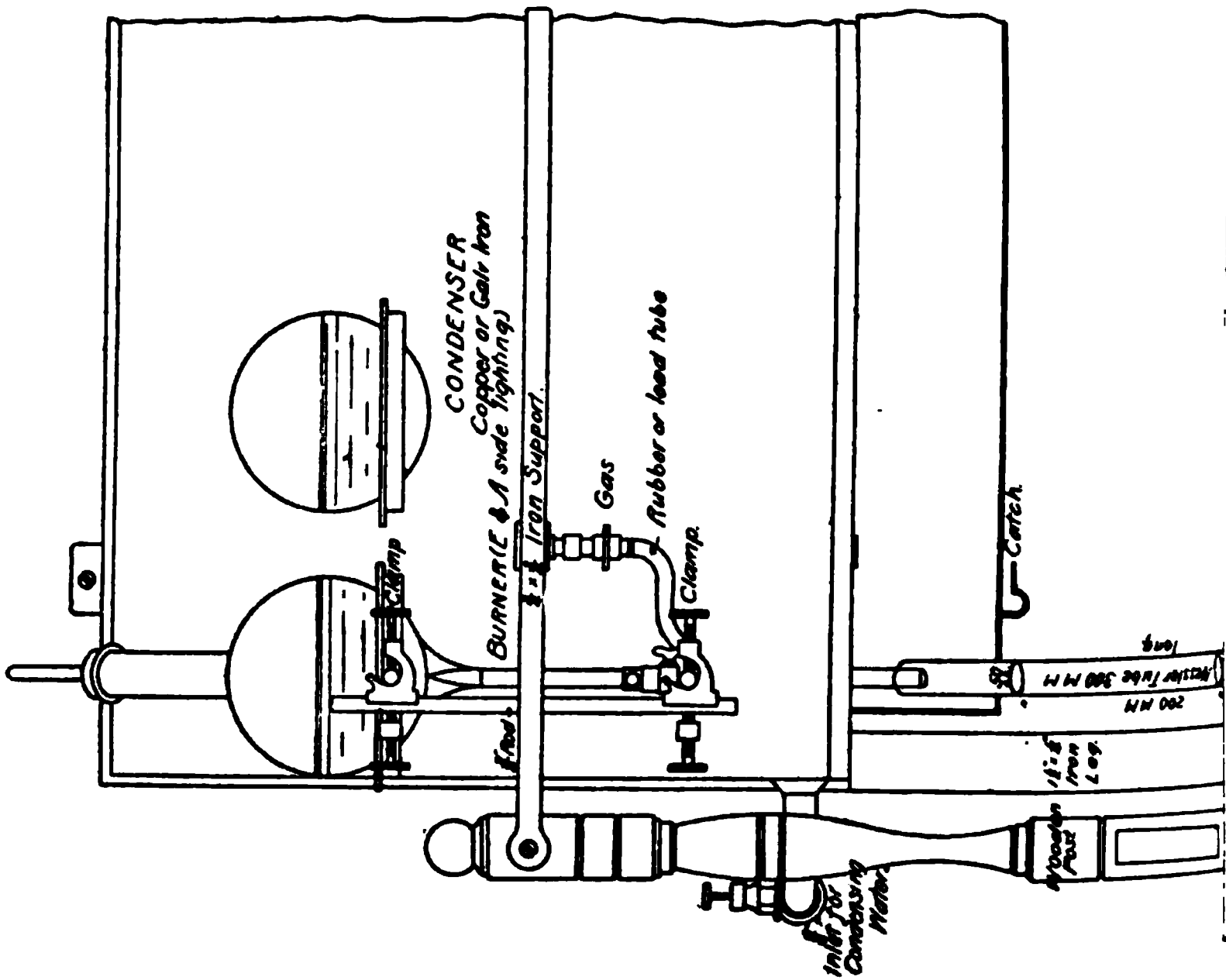
The most important improvements in the construction of sets of stills were made by the chemists of the United States Department of Agriculture, and are described by Professor S. W. Johnson in Bulletin No. 10 of the Division of Chemistry.

This apparatus,<sup>3</sup> of course, is well known and possesses the advantage that it can be operated from one side of the condenser tank. The distilling flasks are raised above the bench, so that it is possible to reach under them for the purpose of attending to the receiving flasks. The distilling flasks are supported upon

<sup>1</sup> "Water Analysis," New York, 1899.

<sup>2</sup> Wiley: "Agricultural Analysis," Vol. II, 203.

<sup>3</sup> *J. Anal. Chem.*, 4, 179; also Wiley: *loc. cit.*, 208.



on an iron shelf. They are joined to the helical block-tin condenser tubes by a safety bulb and rubber connectors. This apparatus was adapted to water analysis by Hazen and Clark.<sup>1</sup>

This apparatus was further improved by the chemists of the Massachusetts Board of Health by bringing the condensing tubes out above the open top of the condenser tank, and by connecting them directly with the stoppers of the distilling flasks, thus avoiding a rubber connection between the distilling flask and the condenser tube. This apparatus was used by the writer for several years, and was found to be quite convenient; nevertheless, some improvements suggested themselves during that time, and in designing a group of ten stills the form described below was developed.

The distilling flasks of the Johnson apparatus are supported on an iron distilling shelf, and the burners are supported on another shelf placed beneath. The metal shelves are hard to keep clean and are, of course, non-adjustable. The distilling flasks, moreover, are placed vertically, and the contents are more liable to be projected into the condenser on that account than if they are inclined. The condenser is unnecessarily large, and the receiving tubes are placed so far under the apparatus as to be inconvenient to tend.

The apparatus described below was designed to overcome the faults of the older apparatus. The drawing on page 470 shows the construction quite plainly. Any desired number of stills can be provided for.

#### CONDENSER TANK.

The condenser tank is built of copper or galvanized iron. The galvanized iron should be japanned. It is inclined so as to bring the lower ends well forward, and is 7.2 inches in length for each unit. The tank is 3.5 inches thick, and is rhomboidal in section, with sides 25 inches and 4.25 inches long respectively. The condenser tubes are of block tin  $\frac{3}{8}$  inches in diameter and about 36 inches long. They are straight, not helical. They are soldered into the bottom of the condenser tank, projecting 2 inches below the bottom of the same. They are not supported

<sup>1</sup> Report of Massachusetts Board of Health on "Purification of Water and Sewage," 1890, p. 710.

except at the bottom of the tank, and are sufficiently pliant to allow connection with the flasks to be made with ease.

A swinging gutter is attached to the bottom of the condenser. This gutter can be swung under the condenser tubes when "boiling out" the apparatus. A small upturned gutter is fashioned around the bottom of the tank to catch any possible condensation. The inclined tank brings the tubes well within reach. The tank is supported by legs to the bench and by lugs to the wall.

#### DISTILLING STAND.

The whole system of flasks and burners is supported by means of a cross bar resting on two or more posts. The  $\frac{3}{4}$  inch square, iron cross bar is drilled with holes  $7\frac{1}{4}$  inches apart, and  $\frac{3}{8}$  inch rods, 10 inches long, are driven into the holes. These rods project 6 inches above and 4 inches below the cross bar. Double clamps hold the rods for the burners and the 5 inch retort stand rings. The base of a Bunsen burner (E and A side lighting) is unscrewed and the burner itself is fitted with a  $\frac{3}{8}$  inch rod. The above arrangement permits the flask and the burner to be moved (within limits) in any direction and at will. The flasks are supported by rings of asbestos ( $\frac{1}{8}$  inch thick,  $6\frac{1}{4}$  inches outside diameter, and  $4\frac{1}{2}$  inches inside diameter); these asbestos rings in turn are supported by the iron rings, being secured to the latter by wires. This furnishes a very neat and springy support for the flasks, and one which, to a great extent, relieves the jar due to bumping and the consequent breaking of flasks. A water supply is provided for the condenser, entering near its bottom at one end and wasting near its top at the opposite end. All parts of the apparatus are accessible, and the flasks can be connected and disconnected with one hand, the spring of the condenser tubes helping to hold the stoppers in place.

The gas pipe is supported on the backs of the wooden posts and  $\frac{3}{8}$  inch hose cocks are placed to the right of each still support; these cocks are connected with the burners by lead or rubber tubes. Either antimony rubber or selected cork stoppers can be used, the latter, perhaps, to be preferred. The ends of the condenser tube pass directly through the stoppers. If desirable, copper flasks can be used. The writer prefers to use the standard 1-liter, Jena glass round-bottomed flask.

For the determination of nitrogen by the Kjeldahl method it is best to connect the ends of the condenser tubes with glass tubes, the latter to dip into standard acid contained in the receiving vessels. Safety bulbs may also be placed at the tops of the distilling flasks connecting the same with the condenser tubes.

The first set of stills of this design was built for the laboratory of the Cincinnati Water Commission in 1898. It consisted of two units. Since that time three other sets have been built, all of which give satisfaction.

To determine the free and albuminoid ammonia in sands and in sewage, it has been found most convenient to place them in a 250 cc. Kjeldahl flask, and to pass through them, by means of a glass tube which should extend nearly to the bottom of the flask, steam from ammonia-free water. This ammonia-free steam is best generated in a closed copper vessel placed at one side of the condenser tank and heated by a large burner. The steam is conducted along the top of the condenser in a  $\frac{1}{2}$  inch metal pipe. At suitable intervals  $\frac{1}{2}$  inch tees with metal cocks are placed, from which steam can be taken for sand and sewage work.

If desirable, the burners can be easily removed and smaller rings can be used to support the Kjeldahl flasks.

Reagents are added to the flasks by means of a long-stemmed funnel.

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### A PROCESS FOR THE DETERMINATION OF CARBON DIOXIDE IN CARBONATES.

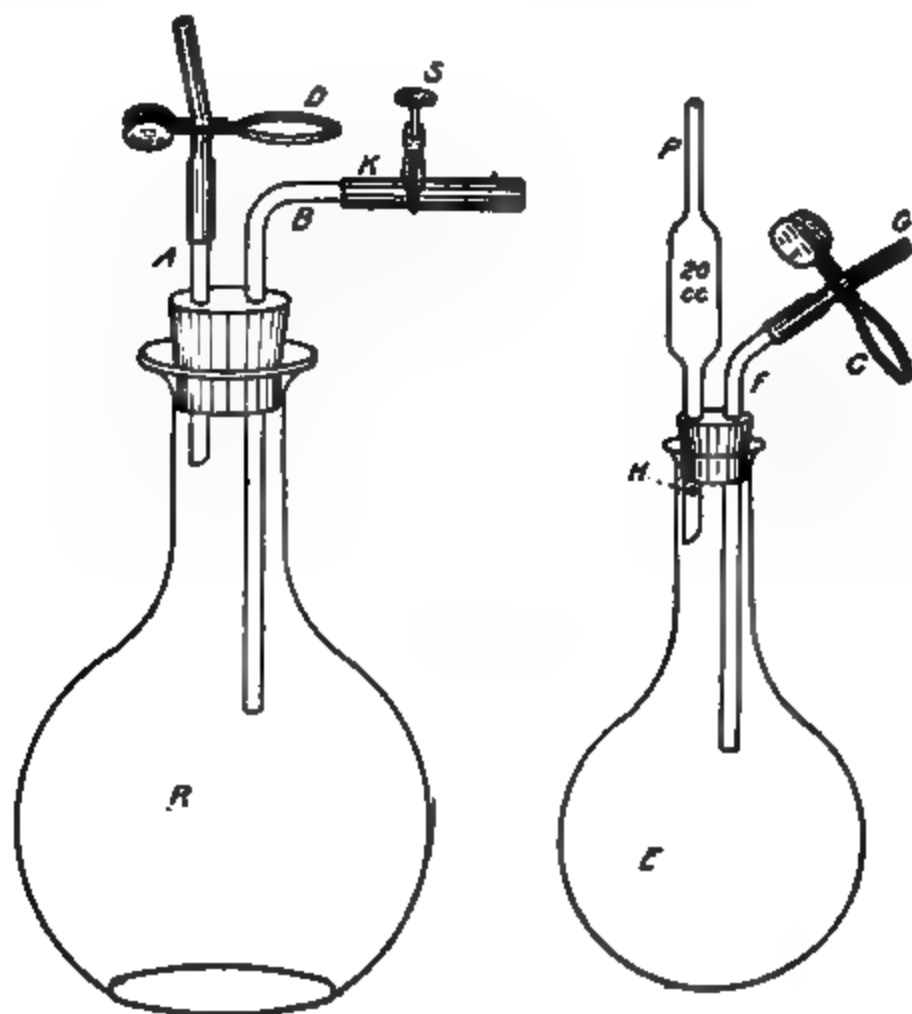
By R. E. DIVINK.

Received May 28, 1900.

THIS process is based on the principle of Pettenkofer's process; namely, absorption of the carbon dioxide by a measured amount of standard baryta water (solution of barium hydroxide), and titration of the excess of the latter with a standard acid. The apparatus about to be described is simple in construction and may be assembled from materials available in almost every laboratory, and the process, if carried out with a reasonable amount of care, should yield fairly accurate results with anyone. It does not require the time and experience necessary in order to obtain good results by the ordinary gravimetric method.

The apparatus consists of a round-bottomed evolution flask E of about 300 cc. capacity, fitted with a rubber stopper and two tubes P and F, and as a receiving flask a 1 quart Bunsen filtering flask R fitted with two tubes A and B.

P is a 20 cc. pipette cut off so as to leave about 3 inches on each side of the bulb. The lower end is ground to a point on an ordinary grindstone, and at about 1 inch above the point there is



a small hole, H, blown into the side of the tube which enables the condensed drops of liquid to fall freely from the end.

F is a tube bent sufficiently to clear the bulb on P, projecting lower into the flask than P, and fitted on the upper end with a short piece of rubber tube G and a pinch-cock C.

The tube B of the receiving flask is fitted with a piece of heavy pressure tubing K, and a screw-cock S. Tube A is fitted with a short piece of soft tubing and a pinch-cock D.

The empty receiving flask R is first placed on a steam-bath in a place free from draughts and steam generated in a small flask or can (I use an ether can) is passed through A until the flask



is hot, and steam issues through B quite freely. S is now closed tightly, then D, and the apparatus disconnected from the source of steam and placed where it may cool. The evolution flask is now connected with the source of steam at G, and, after the air is expelled and steam issues strongly through P, the rubber tube K of the receiving flask is forced on P, then C is closed and the source of steam disconnected; the apparatus after a minute's cooling is ready to receive the carbonate. This is introduced by placing a small cut-off funnel in the end of G, washing 1 gram of the finely pulverized carbonate into the funnel, then by cautiously opening the pinch-cock C, the carbonate may be completely washed into the flask.

The screw-cock S is now opened wide. Twenty-five cc. of 10 per cent. sulphuric acid<sup>1</sup> are now allowed to flow on the carbonate and E is then heated over a low flame to boiling and boiled until the tube G which has been collapsed by the external pressure swells out nearly to normal size. S is then closed tightly and the heat removed. During the boiling E is allowed to hang supported only by the heavy tube K of the receiving flask. This tends to lessen in great measure the force of bumping in E which takes place as soon as the carbon dioxide is nearly boiled out of the liquid. The boiling must, however, be continued for some time in order to completely displace the carbon dioxide in E by aqueous vapor; E is now disconnected from R at K, and after three or four minutes' cooling 500 cc. of the standard baryta water are allowed to flow into R. This is accomplished without contact with the carbon dioxide of the air in the following manner: An ordinary graduated half-liter flask is fitted with a rubber stopper having three holes. Through one of these passes a tube to the bottom of the flask after the manner of a wash-bottle but fitting closely to the flask so as to remove the contents completely. Through another hole passes loosely a short tube connecting with a wash-bottle containing strong caustic potash solution for washing the air admitted to the flask. Through the remaining hole passes a short tube connecting by means of a long rubber tube fitted with a pinch-cock with a bottle of distilled water on a shelf. The standard baryta solution is of

<sup>1</sup> If the substance forms insoluble sulphates use tartaric acid.

such a strength that 500 cc. require 48 to 50 cc. of half-normal hydrochloric acid for neutralization.

The stopper and tubes are first removed from the measuring flask which is filled with air free from carbon dioxide, and it is then quickly filled to the mark by the siphon on the stock baryta bottle. The stopper is then replaced and the siphon of the measuring flask connected with K of the receiving flask. By opening the screw-cock S the baryta water flows into R. S is closed as the last drops enter the siphon of the measuring flask, the tube connecting with the wash-bottle pulled out of the stopper, and 20 cc. or 30 cc. of distilled water allowed to flow into the flask. This is then sucked over after replacing the wash-bottle connection, and then 20 or 30 cc. more distilled water sucked over in like manner, taking care that not much air enters R which is now shaken thoroughly, and after a minute or two washed air is allowed to enter. The flask is then shaken occasionally for about ten minutes, then air allowed to enter, disconnected from the measuring apparatus, the tubes and stopper rinsed quickly with the jet of distilled water and then immediately titrated with half-normal hydrochloric acid with phenolphthalein as indicator. The acid must not be run in too quickly and the contents of the flask must be thoroughly agitated while the acid is run in so as to avoid decomposition of barium carbonate with loss of carbon dioxide and consequent lowering of the result. The whole process including the standardizing of the baryta solution, weighing the carbonate, etc., can be quite expeditiously carried out and the results are as accurate as those of most technical processes. In working with C. P. sodium carbonate, I have obtained the following figures: 41.33, 41.42, 41.51, 41.32, 41.37, 41.34, and 41.36 per cent. Theory requires 41.51 per cent. Some trials with barium carbonate gave 21.99, 22.05, 21.98, and 21.91 per cent. Theory requires 22.33 per cent.; the barium carbonate contained quite a little chlorine. In this case tartaric acid was used to decompose the carbonate.

Freshly precipitated barium carbonate is sufficiently soluble to give a very faint alkaline reaction to the liquid, and this must be borne in mind if the color returns faintly after titrating.

BUFFALO, May 25, 1900.

[A CONTRIBUTION FROM THE LABORATORY OF THE OMEGA PORTLAND CEMENT CO., JONESVILLE, MICH.]

## A METHOD FOR THE RAPID GRAVIMETRIC ESTIMATION OF LIME.

BY W. H. HESS.

Received May 26, 1900.

**A**N accurate gravimetric determination of lime in cement materials is very important as a check on the calcimeter. The method whereby lime is precipitated as the oxalate, ignited and weighed as the oxide, is both tedious and uncertain since prolonged ignition at a very high temperature is required to completely remove all the carbon dioxide.

The following method of estimation in which the lime is weighed as the sulphate has been found to be rapid and accurate.

The lime in the sample is precipitated and separated as the oxalate in the usual way, and the ignition is carried to the point of removing the filter from the residue of lime. The crucible is allowed to cool partially, when a portion of chemically pure ammonium nitrate, approximately equal in bulk to the lime in the crucible, and about twice as much chemically pure fused ammonium sulphate are added. A tight fitting cover is now placed on the platinum crucible and then gentle heat is applied. It has been found very convenient to incline the crucible at an angle of about  $30^{\circ}$ , allowing the tip of the crucible cover to project outward and then apply the flame to the tip of the cover gradually bringing the flame under the crucible as the reaction grows less and less violent. The reaction is complete when fumes of ammonia salts are no longer driven off. Intense ignition is unnecessary and is to be avoided. The crucible should be weighed with its cover.

It was found that if ammonium sulphate alone was used, the transposition of carbonate to sulphate of lime was not always complete on first treatment. By the use of ammonium nitrate the easily fusible nitrate of lime is first formed, which is then completely transposed to the sulphate. The ammonium nitrate also helps to complete the ignition of the filter if any remains unburned.

Results on known samples of pure calcium carbonate are as follows :

Weight of CaCO <sub>3</sub> taken. Grams.	Weight of CaCO <sub>3</sub> recovered. Grams.
0.5003	0.4998
0.4997	0.4993
0.5012	0.5007
0.8472	0.8465
1.0037	1.0026

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**ON A SYSTEM OF INDEXING CHEMICAL LITERATURE;  
ADOPTED BY THE CLASSIFICATION DIVISION  
OF THE U. S. PATENT OFFICE.<sup>1</sup>**

BY EDWIN A. HILL.

Received May 12, 1900.

IN the following paper I will endeavor to describe the system of indexing or digesting chemical literature and patents, now in use in the Classification Division of the United States Patent Office. This division was organized about a year ago to perfect the existing classification of United States patents. Under our laws, no valid patent can be granted for any new process, composition of matter, or chemical body, described in any printed publication prior to the inventor's discovery thereof, or more than two years prior to the date of his application for such patent ; and, among other things, this division is now preparing an index or digest of literature and patents relating to chemical bodies and processes, for the use of the office in making its examinations of pending applications.

The system adopted is in the nature of a reference index rather than a classification, and is one elaborated by myself, some five or more years since for another purpose, and on which we have been at work since last summer. I may add that our work was well advanced before my attention was called to the fact that there are great similarities between this system and that of Richter.

Generally speaking, in any comparison of digests or indexes that system may be considered best which, in the simplest, most certain, and most direct manner, puts the inquirer in possession of the desired information.

<sup>1</sup> Read before the Washington Section of the American Chemical Society, May 10, 1900.

## INDEXING CHEMICAL LITERATURE.

If chemical bodies each had but one instead of many names and if, in chemical literature, one never met with bodies as unchristened, then undoubtedly, the dictionary plan, pure and simple, in which the names of bodies were alphabetically ranged and the references to literature and patents were collected under their proper titles, would answer every requirement, and would be, in fact, the only proper system to use.

Practically however, most bodies known to chemists have more than one name, many have several, and the names approved in prior decades are generally not the names in highest repute to-day; nor is it likely that the names now in use will in the future or even in most cases, remain those approved in future years.

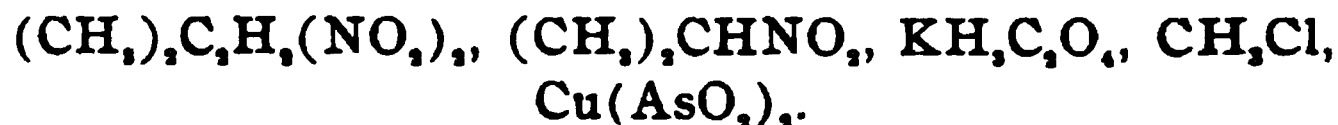
Where a chemical compound has several names, were it possible to decide now (which perhaps might be done) which of them was, on good scientific grounds, the most appropriate in view of present knowledge, and further (which, of course could not be done), could one be assured that such name would remain the approved name for all future time, such title could without hesitation, be now adopted as the indexing title, under which all references to literature or patents could be entered, and all other titles and names cross-referenced into it; but while this might be done now in certain cases, who can guarantee that all the names approved to-day shall retain that approbation as our knowledge of chemical constitution is increased?

Evidently the dictionary plan, unmodified, is not the best, some better system must be devised not open to these objections.

It would seem that the kind and number of the component atoms of a chemical compound are its most unvarying characteristics, and are subject only to the errors of chemical analysis; and that therefore, these must form the most stable basis for any general scheme for the indexing or digesting of chemical literature; and this conclusion appears to have been independently reached by others than myself; as, for example, by Richter in his recent and former work, and by Jacobsen and Steitz following Richter in the index numbers of *Berichte* for 1898 and 1899. We differ chiefly in the methods by which this principle receives practical application.

The simplest, most certain, and most direct system would be to recast the empirical formulas of the compounds, writing

the atoms in the alphabetical order of their chemical symbols, and to then arrange the formulas on an alphabetical basis. For example, take the bodies



Rewriting them as above, and arranging them alphabetically, we have



It should be noted, however, that the compounds containing C and H, and broadly included in the domain of organic chemistry, constitute so large and important a class that we are fully justified in departing slightly from the alphabetical arrangement of chemical symbols, in order to thereby bring more closely together in the index bodies more or less closely related.

Generally speaking, an attempt to combine a dictionary or digest with a classification will be disastrous. We cannot sit on two stools at once, we will surely fall between them; and too much classification grafted on the dictionary or digest idea will give what is neither a good digest nor a good classification.

Classification, as applied to chemical compounds, should be supplementary to, and independent of, a mere digest or reference index.

In practice, therefore, I have modified the purely alphabetical scheme, and have adopted the following general rule for indexing:

*Reject the water of crystallization, and rewrite the empirical formula in the alphabetical order of the chemical symbols, except that in carbon compounds write C first and H second; follow this rewritten formula with the constitutional formula, when given, adding the water of crystallization, if any, but arrange the titles alphabetically by the rewritten formula.*

The reason for disregarding water of crystallization may be illustrated as follows: the three bodies,  $\text{Na}_2\text{SO}_4$  or anhydrous sodium sulphate,  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$  or Glauber's salt, and the heptahydrated salt  $\text{Na}_2\text{SO}_4 + 7\text{H}_2\text{O}$ , are in this way all indexed under the same indexing formula  $\text{Na}_2\text{O}_4\text{S}$ , and are thereby brought closely together, as they should be, in one place in the digest. If on the other hand water of crystallization was taken

into account for indexing purposes, the corresponding index formulas would become  $\text{Na}_2\text{O}_4\text{S}$ ,  $\text{H}_{20}\text{Na}_2\text{O}_{14}\text{S}$ , and  $\text{H}_{14}\text{Na}_2\text{O}_4$ , respectively, and these three very closely related bodies would in consequence, be widely separated in the digest, which result would, we think, be a very undesirable one.

Our index is being prepared on the card catalogue plan. The cards used are the regular Library Bureau standard card, N 33, size  $7\frac{1}{2}$  by  $12\frac{1}{2}$  cm., or approximately 3 by 5 inches, with no rulings except a single blue horizontal line, ruled  $\frac{1}{8}$  of an inch below the top edge of the card.

The following is a sample set of cards as actually made out in a given instance, except in size.

ONE FORMULA CARD:

$\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$                       or                       $(\text{CH}_3\text{CO}_2)_6\text{Fe}_2$ .  
 Ferric Acetate; Acetate of Iron;  
 Klaproth's Iron Tincture; Tinctura  
 Ferri Acetatis; Iron Tincture,  
 Klaproth's.  
 See A Treatise on Chemistry. By H. E.  
 Roscoe and C. Schorlemmer, Vol. 3, Or-  
 ganic Chemistry, Part I, Page 505.

ONE POLYMER OR MULTIPLE FORMULA CARD:

$\text{C}_6\text{H}_9\text{FeO}_6$                       Polymer                      Class 2.  
 See  $\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$  or  $(\text{C}_6\text{H}_9\text{FeO}_6)_2$   
 Ferric Acetate.

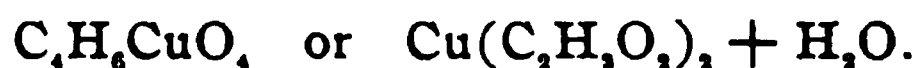
TWO CLASSIFICATION CARDS:

Acetates  
Ferric.  
 See  $\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$  or  $(\text{CH}_3\text{CO}_2)_6\text{Fe}_2$ .  
Iron  
Acetate of.  
 See  $\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$  or  $(\text{CH}_3\text{CO}_2)_6\text{Fe}_2$ .

FOUR SUBJECT-MATTER OR TITLE CARDS:

Ferric Acetate  
See  $\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$ .  
Klaproth's Iron Tincture  
See  $\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$ .  
Iron, Klaproth's Tincture of  
See  $\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$ .  
Tinctura Ferri Acetatis  
See  $\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$ .

Considering first the formula card, it will be noted that in the formula the atoms are rearranged in the alphabetical order of their chemical symbols, except that in carbon compounds C comes first, and H second; and that, had there been water of crystallization in the formula, it would have been rejected. Then follows the constitutional formula, where the water of crystallization, if any, would appear. Thus had the body been cupric acetate, the first line of the formula card would have been



Then follows under the blue ruling, all the names given for the body in question, and finally the reference, by volume and page, to the work indexed.

When a citation is to a patent instead of to a book or other printed work, the reference given will be about like this:

See U. S. Patent No. 319082 to Fahlberg, dated June 2, 1885.

The arrangement of these cards in the card index is strictly an alphabetical one. Thus, all cards reading C<sub>1</sub> take precedence of C<sub>2</sub>, C<sub>3</sub>, of C<sub>4</sub>, etc., etc. In the series C<sub>1</sub>, etc., the order of arrangement would be:

CAgNO; CAgS; CAg<sub>2</sub>O<sub>3</sub>; CBr; CClHgN; CCl<sub>2</sub>O; CCl<sub>4</sub>; CCuN; CHAgO<sub>2</sub>; CHBr; CHCl<sub>2</sub>I; CHCl<sub>3</sub>; CH<sub>2</sub>AgNO<sub>3</sub>S; CH<sub>2</sub>Cl<sub>2</sub>; CH<sub>2</sub>S; CH<sub>2</sub>AsCl<sub>3</sub>; CH<sub>2</sub>Br; CH<sub>2</sub>ClOP; CH<sub>2</sub>F; CH<sub>2</sub>; CH<sub>2</sub>AsClO; CH<sub>2</sub>ClN; CH<sub>2</sub>AlNO<sub>3</sub>S<sub>2</sub>; CH<sub>2</sub>ClN; C<sub>2</sub>H<sub>2</sub>; C<sub>2</sub>H<sub>2</sub>CaClO<sub>2</sub>; C<sub>2</sub>H<sub>2</sub>AgNO; C<sub>2</sub>H<sub>2</sub>As; C<sub>2</sub>H<sub>2</sub>AgNO<sub>3</sub>; C<sub>2</sub>H<sub>2</sub>O; C<sub>10</sub>H<sub>11</sub>Cl<sub>2</sub>P; C<sub>22</sub>H<sub>11</sub>ClN<sub>4</sub>O; C<sub>40</sub>H<sub>11</sub>N<sub>4</sub>O<sub>11</sub>S<sub>2</sub>; CdO<sub>4</sub>S; ClCu; ClH<sub>2</sub>Hg<sub>2</sub>NO; DiN<sub>2</sub>O<sub>3</sub>; HKO<sub>2</sub>S; KMnO<sub>4</sub>; PCl<sub>3</sub>; PCl<sub>5</sub>, etc., etc.

The foregoing series will fully illustrate the method of arrangement.

The polymer or multiple formula cards perform the following function: There are many bodies which analysis shows to be composed of certain elements in certain proportions, but for which theory at present indicates a formula containing two, three, or more times as many atoms. Thus at one time the formula of ferric chloride was written FeCl<sub>3</sub>, whereas it is now very often written Fe<sub>2</sub>Cl<sub>6</sub>, and such doubled and tripled formulas are very common.

In all cases where, in the formula as written, the exponents of



all the atoms have a common divisor, after the doubled, tripled, or other form as found is used for preparing the formula card, the formula is then reduced to its lowest terms by dividing the exponents by their greatest common divisor, and a polymer or multiple formula card, made out in the form shown by the foregoing sample ("Class 2," "Class 3," etc., on the polymer cards, indicates the common divisor). In this way the index is rendered independent of any changes in the formula consequent upon future changes of view with reference to constitutional formulas and other matters of theory.

A mere reference index or digest should in no way depend upon any theory subject to future changes with advancing knowledge. Classification, on the other hand, must necessarily depend on theory, and must change as knowledge is increased.

These polymer cards are sorted in with the regular formula cards to form part of the formula division of the index or digest. We may illustrate the function of these cards thus: suppose ferric chloride had been found in the literature under the formula  $\text{Fe}_2\text{Cl}_6$ , and so indexed, but no polymer card made out, and some one consulted the index under the formula  $\text{FeCl}_3$ ; the reference, though in the digest, would not be found, but with the polymer card made out the inquirer by it would be referred to the card  $\text{Fe}_2\text{Cl}_6$ , where the required references would appear. All the remaining cards compose the subject-matter or title index, comprised first of the classification cards, second of the regular subject-matter or title cards, and third of any general topics that it may be thought advisable to include in the alphabetical division of the index.

These cards require but little explanation, except that the general statement should be made that all references to the literature or patents of chemical bodies are intended to be entered on the formula card, and all the other cards are merely used as cross references, referring the inquirer to the formula card for all required information.

Classification, it will be noted, is attempted only to a limited extent now, but will be carried out much more completely hereafter, by a supplementary scheme not yet fully perfected— independent of, though based on, the reference index.

The present scheme however, it will be observed, does inci-

dentally, bring together very many closely related carbon and other compounds, and arranges alphabetically, under such general titles as acids, alcohols, ethers, acetates, chlorides, etc., the specific bodies of the given class.

In practice, to use the digest, if the empirical formula of any compound is known, it must be rewritten by the rule already given, and at once is disclosed the definite place in the formula index where the desired references, if digested, will be found entered upon the formula card.

If on the other hand, one of the various names of the body is given, the subject-matter index is entered alphabetically, and a cross reference obtained to the rewritten formula with which the formula index is entered for the required information.

The question arises, as between this system and such a one as that adopted in the *Berichte*, which one of them is the best; that is, the most practical for the intended uses. It may be said generally that the Patent Office needs the index for exactly the same purpose as the scientific or practical chemist; *i. e.*, to obtain references to the literature concerning definite chemical bodies, where either the name or the chemical composition or both is given, so that the system best for the one use is probably also best for the other as well.

We consider our system to be preferable, certainly so at least for the patent office, and I may say that it was elaborated and adopted without any knowledge of the work of Richter as followed in the *Berichte* by Jacobsen and Stelzner.

In our system, the arrangement of the formulas is governed by the following general principles in the following order:

- 1st. The number of C atoms
  - 2nd. The number of H atoms
  - 3rd. The alphabetical arrangements of the symbols of the remaining elements (including H in other than carbon compounds).
- } in carbon compounds.

Practically, in indexing, or in using the digest as an index, the only thing to be remembered is, that in carbon compounds C comes first and H second, and that otherwise the rearrangement of formulas and the arrangement of such formulas in the digest is always alphabetically by the symbols, instead of by the names of the component elements.

That the *Berichte* system is much more complex will be seen at once. Other things being equal, we deem that system which is simplest to be the best, provided it achieves a result of equal value. The ideal system, we think, produces the best result with the minimum of labor, both mental and physical.

In rewriting the empirical formula by the *Berichte* or Richter system, one must remember the following arbitrary established order of precedence of certain of the chemical symbols; *viz.*, C, H, O, N, Cl, Br, I, F, S, P, and this both in rewriting the formulas and in entering the table. One must also consider the number of carbon atoms in the compound, the number of different varieties of atoms, and various other things as well.

Thus for example, in the Richter system, the following are the principles which govern, in the order of their relative importance:

- 1st. The number of C atoms.
- 2nd. The number of different kinds of atoms other than C.
- 3rd. The arbitrary arrangement of ten of the component elements in the following order; *viz.*, C, H, O, N, Cl, Br, I, F, S, P, all taking precedence over the remaining elements.
- 4th. The arrangement of all other component elements in the alphabetical order of their chemical symbols.
- 5th. The arrangement of chlorides, bromides, amides, anilides of carbon acids, acetyl and benzoyl derivatives, oximes, phenylhydrazones, etc., under the formulas of their corresponding bases.
- 6th. The arrangement in general, of salts, either under the formulas of their bases, or of their acids.
- 7th. The arrangement of salts of quaternary ammonia bases under the formulas of their corresponding hydroxides.

By way of comparison, I have taken from the pages of the *Berichte* index a number of bodies, with the formulas written and arranged as there shown, and have rewritten and rearranged them on our own classification division plan.

**FORMULAS TAKEN FROM THE BERICHTE INDEX.**

Pages refer to *Berichte*, No. 19, of 1899.

C <sub>1</sub>	CO <sub>2</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>14</sub>	C <sub>15</sub>	C <sub>16</sub>	C <sub>17</sub>	C <sub>18</sub>	C <sub>19</sub>	C <sub>20</sub>	C <sub>21</sub>	C <sub>22</sub>	C <sub>23</sub>	C <sub>24</sub>	C <sub>25</sub>	C <sub>26</sub>	C <sub>27</sub>	C <sub>28</sub>	C <sub>29</sub>	C <sub>30</sub>	C <sub>31</sub>	C <sub>32</sub>	C <sub>33</sub>	C <sub>34</sub>	C <sub>35</sub>	C <sub>36</sub>	C <sub>37</sub>	C <sub>38</sub>	C <sub>39</sub>	C <sub>40</sub>	C <sub>41</sub>	C <sub>42</sub>	C <sub>43</sub>	C <sub>44</sub>	C <sub>45</sub>	C <sub>46</sub>	C <sub>47</sub>	C <sub>48</sub>	C <sub>49</sub>	C <sub>50</sub>	C <sub>51</sub>	C <sub>52</sub>	C <sub>53</sub>	C <sub>54</sub>	C <sub>55</sub>	C <sub>56</sub>	C <sub>57</sub>	C <sub>58</sub>	C <sub>59</sub>	C <sub>60</sub>	C <sub>61</sub>	C <sub>62</sub>	C <sub>63</sub>	C <sub>64</sub>	C <sub>65</sub>	C <sub>66</sub>	C <sub>67</sub>	C <sub>68</sub>	C <sub>69</sub>	C <sub>70</sub>	C <sub>71</sub>	C <sub>72</sub>	C <sub>73</sub>	C <sub>74</sub>	C <sub>75</sub>	C <sub>76</sub>	C <sub>77</sub>	C <sub>78</sub>	C <sub>79</sub>	C <sub>80</sub>	C <sub>81</sub>	C <sub>82</sub>	C <sub>83</sub>	C <sub>84</sub>	C <sub>85</sub>	C <sub>86</sub>	C <sub>87</sub>	C <sub>88</sub>	C <sub>89</sub>	C <sub>90</sub>	C <sub>91</sub>	C <sub>92</sub>	C <sub>93</sub>	C <sub>94</sub>	C <sub>95</sub>	C <sub>96</sub>	C <sub>97</sub>	C <sub>98</sub>	C <sub>99</sub>	C <sub>100</sub>	C <sub>101</sub>	C <sub>102</sub>	C <sub>103</sub>	C <sub>104</sub>	C <sub>105</sub>	C <sub>106</sub>	C <sub>107</sub>	C <sub>108</sub>	C <sub>109</sub>	C <sub>110</sub>	C <sub>111</sub>	C <sub>112</sub>	C <sub>113</sub>	C <sub>114</sub>	C <sub>115</sub>	C <sub>116</sub>	C <sub>117</sub>	C <sub>118</sub>	C <sub>119</sub>	C <sub>120</sub>	C <sub>121</sub>	C <sub>122</sub>	C <sub>123</sub>	C <sub>124</sub>	C <sub>125</sub>	C <sub>126</sub>	C <sub>127</sub>	C <sub>128</sub>	C <sub>129</sub>	C <sub>130</sub>	C <sub>131</sub>	C <sub>132</sub>	C <sub>133</sub>	C <sub>134</sub>	C <sub>135</sub>	C <sub>136</sub>	C <sub>137</sub>	C <sub>138</sub>	C <sub>139</sub>	C <sub>140</sub>	C <sub>141</sub>	C <sub>142</sub>	C <sub>143</sub>	C <sub>144</sub>	C <sub>145</sub>	C <sub>146</sub>	C <sub>147</sub>	C <sub>148</sub>	C <sub>149</sub>	C <sub>150</sub>	C <sub>151</sub>	C <sub>152</sub>	C <sub>153</sub>	C <sub>154</sub>	C <sub>155</sub>	C <sub>156</sub>	C <sub>157</sub>	C <sub>158</sub>	C <sub>159</sub>	C <sub>160</sub>	C <sub>161</sub>	C <sub>162</sub>	C <sub>163</sub>	C <sub>164</sub>	C <sub>165</sub>	C <sub>166</sub>	C <sub>167</sub>	C <sub>168</sub>	C <sub>169</sub>	C <sub>170</sub>	C <sub>171</sub>	C <sub>172</sub>	C <sub>173</sub>	C <sub>174</sub>	C <sub>175</sub>	C <sub>176</sub>	C <sub>177</sub>	C <sub>178</sub>	C <sub>179</sub>	C <sub>180</sub>	C <sub>181</sub>	C <sub>182</sub>	C <sub>183</sub>	C <sub>184</sub>	C <sub>185</sub>	C <sub>186</sub>	C <sub>187</sub>	C <sub>188</sub>	C <sub>189</sub>	C <sub>190</sub>	C <sub>191</sub>	C <sub>192</sub>	C <sub>193</sub>	C <sub>194</sub>	C <sub>195</sub>	C <sub>196</sub>	C <sub>197</sub>	C <sub>198</sub>	C <sub>199</sub>	C <sub>200</sub>	C <sub>201</sub>	C <sub>202</sub>	C <sub>203</sub>	C <sub>204</sub>	C <sub>205</sub>	C <sub>206</sub>	C <sub>207</sub>	C <sub>208</sub>	C <sub>209</sub>	C <sub>210</sub>	C <sub>211</sub>	C <sub>212</sub>	C <sub>213</sub>	C <sub>214</sub>	C <sub>215</sub>	C <sub>216</sub>	C <sub>217</sub>	C <sub>218</sub>	C <sub>219</sub>	C <sub>220</sub>			
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In the foregoing arrangement, the formulas are given in the same order as in the *Berichte*, other formulas which come in between these being omitted; and in the following table these formulas are rewritten and rearranged on the plan which we have adopted, a few formulas not found in the *Berichte* index being added to illustrate the application of our scheme to inorganic bodies.

FORMULAS REWRITTEN AND ARRANGED ON THE PLAN ADOPTED BY THE  
CLASSIFICATION DIVISION, U. S. PATENT OFFICE.

The rewritten formula is in our digest generally followed by the empirical or constitutional formula as usually written by chemists, but from lack of space I have omitted the constitutional formula in many cases in the following table :

C <sub>2</sub>	Not in Berzeli Index.	{	AgCl	{	H <sub>0</sub>	CBrN or Br CN
			AgMnO <sub>3</sub>			CBr <sub>2</sub> N <sub>2</sub> O <sub>4</sub> or C(NO <sub>2</sub> ) <sub>2</sub> Br <sub>2</sub>
			AlH <sub>3</sub> NO <sub>3</sub> S <sub>2</sub> or NH <sub>4</sub> Al(SO <sub>4</sub> ) <sub>3</sub>			CCl <sub>2</sub> O or COCl <sub>2</sub>
			+ 12H <sub>2</sub> O			CCl <sub>4</sub>
			AsH <sub>3</sub> KO <sub>4</sub> or KH <sub>2</sub> AsO <sub>4</sub>			CHBrN <sub>2</sub> O <sub>4</sub> or CHBr(NO <sub>2</sub> ) <sub>2</sub>
			AuCl <sub>3</sub> K or KA <sub>2</sub> AuCl <sub>4</sub>			CHBr <sub>3</sub>
			BNaO <sub>2</sub> or NaBO <sub>2</sub>			CHClO <sub>2</sub> or COCl.OH
			BaN <sub>2</sub> O <sub>6</sub> or Ba(NO <sub>3</sub> ) <sub>2</sub>			CHCl <sub>3</sub>
			{ Br <sub>2</sub> OSe or SeOBr <sub>2</sub>			CHN or HCN
			{ Br <sub>2</sub> Zn or ZnBr <sub>2</sub>			CHNS or CN.SH

C <sub>1</sub>	H <sub>1</sub>	CH <sub>3</sub> I, CH <sub>3</sub> N <sub>3</sub> , CH <sub>3</sub> O or COH <sub>3</sub>	C <sub>6</sub>	H <sub>1</sub>	(
	H <sub>2</sub>	CH <sub>3</sub> Br, CH <sub>3</sub> N <sub>3</sub> , CH <sub>3</sub> O, CH <sub>3</sub> N or NH <sub>2</sub> (CH <sub>3</sub> )		H <sub>2</sub>	(
	H <sub>3</sub>	CO <sub>2</sub> , CS <sub>2</sub>		H <sub>3</sub>	(
	H <sub>4</sub>	C <sub>2</sub> Cl <sub>2</sub> , C <sub>2</sub> Cl <sub>2</sub> Hg <sub>2</sub> or C <sub>2</sub> Hg <sub>2</sub> Cl <sub>2</sub> , C <sub>2</sub> HCl <sub>2</sub> Hg <sub>2</sub> O <sub>2</sub> or CH <sub>2</sub> Cl <sub>2</sub> CO <sub>2</sub> H or CCl <sub>2</sub> CHO		H <sub>4</sub>	(
	H <sub>5</sub>	C <sub>2</sub> Cl <sub>2</sub> CO <sub>2</sub> H or CCl <sub>2</sub> CHO		H <sub>5</sub>	(
C <sub>2</sub>	H <sub>1</sub>	C <sub>2</sub> Cl <sub>2</sub> or C <sub>2</sub> H <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub>	C <sub>7</sub>	H <sub>1</sub>	(
	H <sub>2</sub>	C <sub>2</sub> Cl <sub>2</sub> or CCl <sub>2</sub> CH(OH) <sub>2</sub> or (CH <sub>2</sub> Cl) <sub>2</sub> N <sub>2</sub>		H <sub>2</sub>	(
	H <sub>3</sub>	C <sub>2</sub> Cl <sub>2</sub> or CHO.CH(SO <sub>2</sub> H) <sub>2</sub>		H <sub>3</sub>	(
	H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> N <sub>2</sub> , C <sub>2</sub> H <sub>2</sub> NO <sub>2</sub> or C <sub>2</sub> H <sub>2</sub> NO <sub>2</sub> , C <sub>2</sub> H <sub>2</sub> BrN or N(CH <sub>2</sub> ) <sub>2</sub> Br, C <sub>2</sub> H <sub>2</sub> O <sub>2</sub> S or C <sub>2</sub> H <sub>2</sub> (SO <sub>2</sub> H) <sub>2</sub>		H <sub>4</sub>	(
	H <sub>5</sub>	C <sub>2</sub> H <sub>2</sub> I <sub>2</sub> , C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub> or N=C-N-N         H-N-C-CO-O		H <sub>5</sub>	(
C <sub>3</sub>	H <sub>1</sub>	CHO.C <sub>2</sub> H <sub>5</sub>	C <sub>8</sub>	H <sub>1</sub>	(
	H <sub>2</sub>	C <sub>3</sub> H <sub>3</sub> Cl <sub>2</sub> or C <sub>3</sub> H <sub>3</sub> NO <sub>2</sub>		H <sub>2</sub>	(
	H <sub>3</sub>	C <sub>3</sub> H <sub>3</sub> BrN or N(CH <sub>2</sub> ) <sub>2</sub> Br, C <sub>3</sub> H <sub>3</sub> O <sub>2</sub> S or C <sub>3</sub> H <sub>3</sub> (SO <sub>2</sub> H) <sub>2</sub>		H <sub>3</sub>	(
	H <sub>4</sub>	C <sub>3</sub> H <sub>3</sub> I <sub>2</sub> , C <sub>3</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub> or N=C-N-N         H-N-C-CO-O		H <sub>4</sub>	(
	H <sub>5</sub>	CHO.C <sub>2</sub> H <sub>5</sub>		H <sub>5</sub>	(
C <sub>4</sub>	H <sub>1</sub>	C <sub>4</sub> H <sub>4</sub> Cl <sub>2</sub> or C <sub>4</sub> H <sub>4</sub> NO <sub>2</sub>	C <sub>9</sub>	H <sub>1</sub>	(
	H <sub>2</sub>	C <sub>4</sub> H <sub>4</sub> BrN or N(CH <sub>2</sub> ) <sub>2</sub> Br, C <sub>4</sub> H <sub>4</sub> O <sub>2</sub> S or C <sub>4</sub> H <sub>4</sub> (SO <sub>2</sub> H) <sub>2</sub>		H <sub>2</sub>	(
	H <sub>3</sub>	C <sub>4</sub> H <sub>4</sub> I <sub>2</sub> , C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> or N=C-N-N         H-N-C-CO-O		H <sub>3</sub>	(
	H <sub>4</sub>	CHO.C <sub>2</sub> H <sub>5</sub>		H <sub>4</sub>	(
	H <sub>5</sub>	CHO.C <sub>2</sub> H <sub>5</sub>		H <sub>5</sub>	(
C <sub>5</sub>	H <sub>1</sub>	C <sub>5</sub> H <sub>5</sub> Cl <sub>2</sub> or C <sub>5</sub> H <sub>5</sub> NO <sub>2</sub>	C <sub>10</sub>	H <sub>1</sub>	(
	H <sub>2</sub>	C <sub>5</sub> H <sub>5</sub> BrN or N(CH <sub>2</sub> ) <sub>2</sub> Br, C <sub>5</sub> H <sub>5</sub> O <sub>2</sub> S or C <sub>5</sub> H <sub>5</sub> (SO <sub>2</sub> H) <sub>2</sub>		H <sub>2</sub>	(
	H <sub>3</sub>	C <sub>5</sub> H <sub>5</sub> I <sub>2</sub> , C <sub>5</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub> or N=C-N-N         H-N-C-CO-O		H <sub>3</sub>	(
	H <sub>4</sub>	CHO.C <sub>2</sub> H <sub>5</sub>		H <sub>4</sub>	(
	H <sub>5</sub>	CHO.C <sub>2</sub> H <sub>5</sub>		H <sub>5</sub>	(
C <sub>6</sub>	H <sub>1</sub>	C <sub>6</sub> H <sub>6</sub> Cl <sub>2</sub> or C <sub>6</sub> H <sub>6</sub> NO <sub>2</sub>	C <sub>11</sub>	H <sub>1</sub>	(
	H <sub>2</sub>	C <sub>6</sub> H <sub>6</sub> BrN or N(CH <sub>2</sub> ) <sub>2</sub> Br, C <sub>6</sub> H <sub>6</sub> O <sub>2</sub> S or C <sub>6</sub> H <sub>6</sub> (SO <sub>2</sub> H) <sub>2</sub>		H <sub>2</sub>	(
	H <sub>3</sub>	C <sub>6</sub> H <sub>6</sub> I <sub>2</sub> , C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> or N=C-N-N         H-N-C-CO-O		H <sub>3</sub>	(
	H <sub>4</sub>	CHO.C <sub>2</sub> H <sub>5</sub>		H <sub>4</sub>	(
	H <sub>5</sub>	CHO.C <sub>2</sub> H <sub>5</sub>		H <sub>5</sub>	(

As a practical test of the two systems, take the six following bodies; rewrite them first by our system and find them in our table; then rewrite them by the *Berichte* rules and find them in the *Berichte* table; and the demonstration of the superior simplicity of our system will be complete. The bodies are:

1. .... SP(OC<sub>6</sub>H<sub>5</sub>)Cl<sub>2</sub>
2. .... C<sub>6</sub>H<sub>2</sub>Cl<sub>3</sub>(OH)
3. .... CHg<sub>3</sub>Cl<sub>3</sub>CO<sub>2</sub>H
4. .... CN.SH
5. .... N.CO.C<sub>2</sub>H<sub>5</sub>.HBr
6. .... 
$$\begin{array}{c} \text{N} = \text{C} - \text{N} - \text{N} \\ | \qquad \qquad \qquad \diagup \qquad \qquad | \\ \text{HN} - \text{C} - \text{CO} - \text{O} \end{array}$$

This comparison speaks louder than words, and I think most chemists will agree with me that our system affords to the inquirer, with the minimum of technical knowledge, the maximum of information, in the surest manner, and with the minimum of mental and physical labor, and without the danger that a future change in theory will mislead the future user of it. In other words, the use of the digest is as far as possible independent of all theory, and founded only on unchanging facts.

Let me here call attention to the point that in the *Berichte* system the formulas of very many large classes of bodies, such as salts, amides, anilides of acids, etc., etc., have no representation in the index. Their formulas do not appear in it at all; but only their names, which are classified under the different formulas of some related body; so that in a given case, unless one remembers all these various classes of excepted bodies, if forgetting any of these things he rewrites the formula, and enters the *Berichte* digest or index with it, thus rewritten, he finds none of the matter indexed. He must first remember that the body sought is not indexed under its own, but under some different formula of a body more or less closely related to it; that is, that the body belongs in some one of these many excepted classes, and then, after determining under what base or acid it will be found, he must enter the table with the rewritten formula, not of the body itself, but of the given base acid or other body to which it is now supposed to be related, although advancing knowledge may hereafter prove this view as to supposed relationship to be erroneous.

Moreover, in the case of a body of which the number and kind of the component atoms are known, but as to the constitution of which little or nothing is known, while the body may be correctly entered in the *Berichte* index under the formula of some base or acid or other supposedly related body, it would evidently never be found, because not knowing its constitution, we do not know the base or acid under which it is indexed, and so would not find it in the table.

In our system, every chemical body indexed is represented in the digest or table by its rewritten empirical formula. No bodies are indexed as subheads under the formulas of other compounds. The indexing, and conversely, the finding of the body in the index, is rendered absolutely independent of any theories of constitution whatever, and made to depend solely on the kind and number of the component atoms, arranged alphabetically by their symbols, except that in carbon compounds, C comes first and H second. Nothing can be more simple.

No serious attempt is made, however, to make the system which is merely intended to be a reference index, at once a classification, and also an index as well; that is, classification is not pushed beyond the point where it begins to encroach on the digest idea; and any such attempt, I believe, will surely fail to fully fulfil either function in the highest degree. In a good index the classification idea must be kept subordinate. Hence, it follows that from our point of view, the *Berichte* system, as a mere digest or index, as well as that of Richter and all other similar systems, is inferior to ours in the points indicated; while as systems of classification, they can not but be inferior to such as are founded on proper lines. Such systems can be worked out without being hampered by the digest or dictionary idea, and which important work — classification proper as distinguished from a mere digest or index — we hope to be able to take up at some future time, on a comprehensive scale, as supplementary to the present work in hand.

It would be manifestly unfair, however, in this comparison of systems, to overlook the fact that both in the field covered, and in the intended use, the two systems are not exactly the same. Richter's system is designed for and applied solely to the bodies of organic chemistry for the use of specialists in that branch.

familiar with its classification. Ours covers the entire domain of chemical research, both inorganic and organic, and is for the general inquirer. From a classification standpoint, the order of preference — C, H, O, N, Cl, Br, I, F, S, P — is justified in organic chemistry; but in inorganic chemistry it has no justification, and would lead to awkward and unfamiliar formulas, with no compensating advantages.

When a general reference index to all bodies, both organic and inorganic, is under consideration, if an order of preference is to be established, one will have to adopt different orders in the organic and inorganic domains, or else do as we have done—that is, establish no order of preference whatever, with the one exception of giving C and H preference in that order in carbon compounds so as to thereby effect a differentiation of organic from inorganic bodies.

Moreover, Richter's system is more adapted to the needs of those who are studying bodies as a class and to whom classification is of greater importance; while our system is specially adapted to the needs and requirements of those who are merely searching for references to the literature of specific chemical bodies—particularly those bodies the empirical formulas of which are known, but as to the constitution of which little if any information is at hand.

The approval of our system, therefore, does not necessarily imply that it is a criticism of or shall supersede that of Richter. Because of these differences in the field covered and in the intended use, the two systems have really no serious quarrel; and where ours is applied to organic bodies, the Richter formula could also be given on the cards prepared on our system to facilitate reference to the *Berichte*, and the Richter Lexicon, with its 75,000 titles of organic compounds.

In conclusion, there arises the question of how far the system described in this paper is adapted to the needs of chemists generally as a universal scheme for the indexing or digesting of chemical literature. That it fully meets the needs of the Patent Office we have no doubt, and for myself, I can not see why the needs of the practical and scientific chemist are not about the same as ours.

The object of a dictionary of chemistry, a reference index, or



a digest system, such as those contained in the German *Berichte* and similar works, and the *Abstracts* of the Chemical Society, is to furnish to the chemical inquirer, in the best and quickest way, digested information and references to the latest literature on any given chemical body, process, or general chemical topic. Our system directly covers, very fully, and in, we believe, the best and quickest way, the inquiry as to the chemical body, and incidentally, the inquiry as to any specific chemical process, since every such process has for its aim the production of a specific chemical body, and hence the literature relating to such process will, of course, be digested under the formula of the resulting product.

An index or digest of general chemical topics, or processes of a general nature not specially adapted to the production of a specific body, but to many bodies more or less closely related, can not, of course, be included in any mere formula scheme, which can only represent specific bodies, but must come into some general or dictionary plan based on names or titles, and such references of this class as it might seem desirable to include in a general scheme of chemical indexing, would easily work in with the alphabetical arrangement of chemical names provided for in the system we have adopted.

Probably the most natural objection which the practical chemist would make to the adoption of the system of indexing by rewritten formulas as one of the component parts of a general scheme for chemical indexing, would be that to rewrite or rearrange the chemical symbols in the accepted formula on a purely alphabetical basis, would appear to offend the chemical sense, and do violence to the long-established usage of chemists in writing such formulas with the component elements or radicals arranged in an order depending largely on their relative, positive, or negative qualities, using these terms in their broadest chemical meaning.

In answer to this objection, it should be noted that if this really be a valid objection, it applies just as fully to the system used by Richter in the earlier editions of his "Lexicon" and adopted and approved in the *Berichte* Indexes and other publications as to ours; and it can be urged with equal force against the monumental work of Richter, just published, which is an

enlarged edition of his earlier work. So that, with such backing as Richter and the *Berichte*, it would seem as if the objection was not as valid as might at first appear.

Moreover, in our system it is an unvarying rule that the rearranged formula is never used or written, whether on cards or elsewhere, without being immediately followed by the empirical or constitutional formulas, so far as the same are known or inferred; so that an objection which might have force, were nothing but the rewritten formulas given in the digest or on the index cards, loses its force when the ordinary formula, so familiar to the chemist, is always an invariable accompaniment of the new and unfamiliar indexing formulas.

As soon as the idea is fully grasped that the rewritten formula is merely an arbitrary arrangement, in the nature of a position indicator, determining position in a mere reference index to literature and nothing more, the chemical sense will be no longer offended. The justification for its use lies in the fact that such a formula unerringly indicates one, and one only, definite and specific place in the index where we are to look for all references, with a certainty that no other character, name, or title of the body can afford. With other systems we are somewhat uncertain where to look for our information;—with this system all uncertainty at once disappears.

Personally I should be glad to see a general scheme of indexing current chemical literature carried out at some future time for the benefit of American chemists, under the auspices, for instance, of the Smithsonian Institution, along these general lines which have been blocked out in our Classification Division, modified or improved perhaps by the combined wisdom and experience of the American Chemical Society.

For example, the Smithsonian Institution might publish an annual index to current chemical literature, divided into a formula division, arranged along some such lines as here suggested, and a subject-matter or title division, in which all names and subjects were alphabetically arranged, and the names of chemical bodies all cross-referenced into the formula index, all references to the literature of chemical bodies being collated under the unvarying formula of the body, and not under one of its various and varying names.

Such an index should cover the leading chemical periodicals—such works as *Berichte* and the *Abstracts* of the Chemical Society, and the more important chemical publications of the year.

The vast army of chemical workers in our universities, laboratories, and corporate and government offices and institutions, state and national, should be enlisted in the work, each willing worker assigned some special publication or portion of same, and be supplied with standard library bureau cards and general instructions; and the cards as prepared sent in to the central bureau established here in Washington, where, after being sorted into place in the receiving cabinets, and with proper editing, they would form the basis from which would be compiled the annual index volume.

These volumes would probably be less of a digest and more of an index than the present *Abstracts* of the Chemical Society or the *Berichte*, and would cover a somewhat different field than either.

Lastly, these annual volumes should be sold at cost price, so as to become a working tool in the hands of all the chemical workers of the country.

I may here briefly refer to a special development of this work now being carried out in our Patent Office Index. We have procured two copies each of the *Berichte* Indexes for 1898 and 1899. The separate titles in the formula portion of these indexes are in most cases small enough to be cut out and pasted on our standard indexing cards and still leave room enough at the top to rewrite the formula on our own plan. We are also considering the application of this system of cutting and pasting from two duplicate copies to the new Richter "Lexicon" with its 75,000 titles, and possibly to the four volumes of the last edition of Watts' "Dictionary," Thorpe's "Dictionary of Applied Chemistry," the yearly abstract volumes of the *Journal of the London Chemical Society*, and such other works of general reference as it may be found advisable.

But to return, in conclusion, to the idea of a central bureau at Washington, supervising the indexing of chemical literature, would not some such plan, properly matured, and carried out to a successful completion, be a work worthy of the great scien-

tific institution of the national capitol, founded expressly for the dissemination of useful knowledge, and be directly in line with their publication in past years, of the indexes to the literature of specific chemical bodies, which has so much redounded to their credit? It seems to me at least that it would be a work worthy of their best endeavor, and of whose great utility there could be no question whatever.

### CAUSE OF THE LOSS IN WEIGHT OF COMMERCIAL PLATINUM, WHEN HEATED UNDER SOME CONDITIONS.

BY ROBERT W. HALL.

Received June 15, 1900.

THE fact that commercial platinum sometimes loses weight when heated has been frequently noticed and experiments made to determine the cause of the loss. This loss has been observed under at least seven conditions.

1. *When platinum is made the cathode for the spark from an induction coil.*—That platinum is dissipated under this condition, was observed by Plücker<sup>1</sup> and very fully described by him. A. W. Wright<sup>2</sup> and others studied the same phenomena. The platinum is dissipated alike in air, in vacuum, and in hydrogen, and the phenomena are regarded as purely physical or mechanical.

2. *When platinum is heated in a Bunsen gas flame, sufficiently, reducing to deposit some carbonaceous matter on the platinum.*—Rémont<sup>3</sup> obtained in this way, in thirty minutes, a deposit weighing 22 milligrams and containing 10 milligrams of platinum. Rémont made some experiments to show that this loss is not due to the heated carbonaceous matter alone. He attributed it to some constituent of the gas.

3. *When platinum is heated in the ordinary smokeless Bunsen flame.*—Some observers note a constant loss under these conditions. Wittstein<sup>4</sup> found such a loss and attributes it to osmium, which he found in the platinum scrap of that time. Stolba<sup>5</sup> found that a platinum crucible lost weight at the rate of 16 milligrams in twelve hours. Stolba remarks that while he

<sup>1</sup> *Ann. Phys. Chem.*, 103, 90 (1858).

<sup>2</sup> *Sill. J. Sci. and Arts*, January, 1877.

<sup>3</sup> *Bull. Soc. Chim.*, 35, 486 (1881).

<sup>4</sup> *Dingler's poly. J.*, 179, 299 (1866).

<sup>5</sup> *Ibid.*, 198, 177 (1870).

does not deny the possible presence of osmium, there would have to be more osmium in the platinum than in the original ore, to account for the continuous losses he observed. Erdmann,<sup>1</sup> with Pettenkofer, had, however, studied the behavior of platinum crucibles in the Bunsen flame and observed the formation of a gray coating, but without loss or gain in weight. Erdmann concludes that the gray coating is due to molecular change in the platinum. Crookes<sup>2</sup> discusses Erdmann's paper and agrees with him.

The writer's experience agrees with that of Erdmann, so far as constancy of weight is concerned. Possibly some of the platinum of commerce about 1866 to 1870 differed in composition from that commonly used. It may be noted here that platinum heated in a flame of hydrogen containing arsine and then strongly ignited, shows the phenomena observed by Erdmann in a very marked degree.

4. *When platinum is very strongly heated in a furnace for firing porcelain.*—Elsner<sup>3</sup> found that platinum burned into porcelain, was entirely dissipated when exposed to the full heat of an oven used for firing porcelain, during the burning of a batch.

Platinum black, however, placed in a small porcelain crucible, under the same conditions, only melted to small globules, with a metallic luster.

5. *When platinum is heated in a combustion tube in air.*—H. Kayser<sup>4</sup> attempted to free air from possible hydrocarbons by passing it over platinum in a glass tube heated externally. He observed phenomena, which he explained by the assumption that the platinum gave up finely divided particles to the air.

6. *When platinum is heated by an electric current.*—That platinum is dissipated when heated in air by the electric current seems to have been discovered first by Thomas A. Edison.<sup>5</sup>

Edison observed that glass, surrounding the wire, became covered with a mirror of what he assumed to be metallic platinum and that when the wire was placed in a bulb and as

<sup>1</sup> *J. prakt. Chem.*, 79, 117 (1860).

<sup>2</sup> "Select Methods in Chemical Analysis," 2nd Ed., p. 681.

<sup>3</sup> *J. prakt. Chem.*, 99, 257 (1866), from *Chem. tech. Mitth.* (Elsner) 7, 36 (1857-1858).

<sup>4</sup> *Ann. Phys. Chem.*, 34 (1888).

<sup>5</sup> *Chem. News*, 40, 152, from *Proc. Am. Ass.*, 1879, 173.

perfect a vacuum as possible produced, the loss ceased. Edison pronounced the action to be purely mechanical.

Nahrwold,<sup>1</sup> in apparent ignorance of Edison's work, repeated part of Edison's experiments and further observed that the metallic coating dissolved in aqua regia, only in part. Nahrwold pronounces no opinion as to the nature of the action.

Berliner<sup>2</sup> endeavored to explain the action. He found that platinum, which had been exposed to air, gave up gas when heated in a vacuum, that while doing so platinum was dissipated, giving a deposit on glass cylinders surrounding the metal and that the dissipation of the platinum ceased, when gas was no longer given off. In hydrogen the behavior was exactly the same as shown by a single successful experiment and Berliner, therefore, concluded that the action was a purely mechanical one caused by the escaping gases.

7. *When platinum is heated before the blast-lamp.*—Beilstein<sup>3</sup> notes that platinum crucibles, both of pure and of less pure platinum, lost weight to an important degree on ignition but that after repeated ignition the loss became less. The writer's experience does not agree with this. For example, in a series of experiments, a crucible which had been used for some years, was ignited nineteen times, under varying conditions, with a total loss of 10.3 milligrams; on being ignited for the twentieth time (see Table B, Experiment 1) it showed a loss of 2 milligrams in thirty minutes,—a greater loss than was observed in any of the preceding experiments. Perhaps if a new crucible had been used for the first experiment of the series, results like Beilstein's, would have been obtained.

The attention of the writer was directed to the subject soon after moving to a new laboratory, by finding that the ordinary platinum crucibles of commerce lost weight so rapidly, when used for the conversion of calcium oxalate into calcium oxide, that even an approximately constant weight could not be reached.

This was the more remarkable, as the burners and general arrangements were the same, as had been used for several years,

<sup>1</sup> *Ann. Phys. Chem.*, 31, 467 (1887).

<sup>2</sup> *Ibid.*, 33, 287 (1888).

<sup>3</sup> Short abstract *Chem. Centrbl.*, 1880, 614. Original in *Z. rusk. chim. obse.*, 12, 1580, not accessible.

with the exception that for a foot-blower, there was substituted a steady blast from a blowing engine, giving a more evenly high temperature.

The gas used was a mixture of retort gas and of the so-called "water-gas" enriched with naphtha gas. It contained about 15 per cent. of carbon monoxide and in this respect resembled the gas, which had been used formerly, without causing any loss of weight in the crucibles.

The loss was not due to the high temperature alone, for the writer has frequently heated crucibles with a steady blast, to the most brilliant "blue whiteness," without loss.

Experiments showed that the loss was not due to dust in the air or gas, acting as a sand-blast, for filtration of the air and gas through cotton-wool made no difference; nor to unusual amounts of the impurities removable by alkalis in the gas, for the losses still continued after a careful purification of the gas by passing it through potassium hydroxide solution and over "soda-lime."

Nor was the loss likely to be due to any peculiarity in the platinum used, for old and new crucibles of soft, comparatively pure platinum and a crucible of a platinum-iridium alloy, gave about the same results. In every case, after heating, the platinum showed a somewhat roughened surface, with a most beautiful silvery luster.

TABLE A.

Soft, commercial "pure" platinum from Eimer and Amend, New York.

No.	Weight of wire before heating.	Weight after heating.	Gas used.	Duration of experiment in minutes.	Loss or gain in milligrams.	Loss per 15 minutes.	Remarks.
1.	2.9085	2.9085	CO	30	0.0	0.00	
2.	2.9085	2.9085	"	30	0.0	0.00	
3.	2.9083	2.9080	"	35	-0.3	0.13	{ Supply of gas insufficient. Some air may have gained access.
4.	2.9080	2.9054	air	30	-2.6	1.30	{ Slight mirror on the glass.
5.	2.9054	2.9022	"	30	-3.2	1.60	{ Slight mirror on the glass.
6.	2.9022	2.8977	"	45	-4.5	1.50	{ Slight mirror on the glass.

No.	Weight of wire before heating.	Weight after heating.	Gas used.	Duration of experiment in minutes.	Loss or gain in milligrams.	Loss per 15 minutes.	Remarks.
7.	2.8977	2.8889	air	90	-8.8	1.46	{ Slight mirror on the glass.
8.	1.7258	1.7137	"	60	-12.1	3.02	{ Mirror. Thinner wire. Higher resistance. Current more easily regulated. Hence heat higher.
9.	1.7137	1.6905	oxygen	60	-23.2	5.80	
10.	1.6905	1.6902	CO <sub>2</sub>	90	-0.3	0.05	{ Mirror. Heat not high. Difficult to regulate current owing to small resistance.
11.	2.8889	2.8716	oxygen	85	-17.3	3.05	
12.	2.8468	2.7165	"	360	-130.3	5.43	{ Glass covered with an almost opaque mirror.
13.	3.0935	3.0939	hydrogen	60	+0.4		{ Hydrogen found to contain some arsine.
14.	2.8714	2.8715	"	90	+0.1		{ Hydrogen free from arsine.

Some experiments were therefore undertaken to answer the question why platinum crucibles sometimes keep a constant weight, when heated in a gas flame, to a temperature very near their melting-point and why they sometimes lose weight, at a rate amounting to a milligram in fifteen minutes.

Wires of the ordinary soft "pure" platinum of commerce, about 40 cm. in length, were placed within a glass tube 78 cm. in length and 3.5 cm. in diameter, closed at each end with caoutchouc stoppers and provided with openings for the introduction and exit of the different gases used.

The platinum wires used were hung on platinum rods and these again hung on copper conducting wires. A stream of the gas used was passed through the apparatus and then the wire was brought to a temperature as near its melting-point as could be done safely, by means of an electric current.

The details of these experiments are given in table A.

The results of these experiments was unexpected.

They show that the loss of weight, in the reducing or neutral gases, carbon monoxide or carbon dioxide, is zero or very slight; that in hydrogen there is a very slight gain, while



in air and oxygen the loss is very rapid, in Experiment No. 12, amounting to 5.4 milligrams in each fifteen minutes. The two experiments with hydrogen, showing an actual gain, are not necessarily in conflict with Berliner's result, since in these two experiments the platinum was cooled in hydrogen, while in Berliner's experiment the platinum was cooled in a vacuum. The following experiments were made, however, and do seem to conflict with Berliner's result. The wires used in Experiments 13 and 14, were heated by the current, for sixty and ninety minutes, respectively, in an atmosphere of carbon dioxide. After this treatment they weighed within 0.05 milligram of the original weights; that is, the differences were within the error of weighing. It may be remarked that Berliner's experiments were qualitative, but he describes the deposit from hydrogen as an "opaque platinum mirror." Berliner's experiments were beautifully planned and no explanation of the apparent conflict suggests itself.

It, therefore, appeared probable from the result of these experiments, that a highly oxidizing gas flame would cause a greater loss of platinum, than a more reducing one.

Experiments were made to test this by placing a platinum crucible in a blast-flame, first high up in the flame, above the point where the maximum temperature could be reached and where the flame should be oxidizing and then bringing it down by steps, nearer the burner, below the zone of maximum temperature, where the flame should be more reducing, under the following conditions.

Two burners, with converging flames were used, a steady blast from a blowing engine, the flame surrounded by perforated clay crucibles, the blast adjusted in each case so as to give the maximum heat, in the particular position; duration of each experiment thirty minutes.

Weight of the platinum crucible, 11.9694 grams.

The following results were obtained:

TABLE B.

No. of Exp.	Distance between bottom of crucible and the burners. cm.	Loss of weight. Mgs.	Loss per 15 minutes. Mgs.	Remarks.
1.	15.5	2.0	1.0	{ Heat below that of four succeeding experiments. Good white heat.
2.	12.5	1.1	0.55	
3.	10.5	0.8	0.40	{ Heat higher than in No. 2.
4.	8.5	0.5	0.25	
5.	7.5	0.5	0.25	{ Heat as high as in No. 3. Heat lower than in No. 5. Seemed about the same as in No. 1.
6.	6.5	0.5	0.25	

In these experiments the loss in weight varied so much more with the position in the flame, than with the temperature, that the latter relation is entirely masked.

In all cases, where the wires lost weight, when heated by electricity in air or oxygen, mirrors were produced on the glass tube.

In Experiment No. 12, table A, the deposit was removed by aqua regia; only part of it dissolved at first in concentrated aqua regia, just as Nahrwold observed. The solution was filtered from the insoluble part, precipitated by ammonium chloride, and the precipitate ignited. The residue weighed 56.3 milligrams. The insoluble portion was ignited and found to weigh 56.4 milligrams. After ignition this residue dissolved in concentrated aqua regia. A further black precipitate was obtained from the alcoholic filtrate from the precipitation of the first aqua regia solution, which weighed 1.3 milligrams. Hence, if it is assumed that the mirror and these three fractions had about the same composition there were recovered in all 114 milligrams out of 130.3 milligrams. Some of the deposit lay on the platinum supports and could not be recovered.

The behavior of the aqua regia solutions was very different from that of 130 milligrams of the original wire.

These experiments show that the loss of weight of commercial platinum heated by the electric current or before the blast-lamp, is due to the chemical action of oxygen, that certain elements are fractioned out of the impure platinum and that the loss of weight is not, as has been suspected, due to the use of "water-

gas'', except in so far as this gas is likely to give a hot and strongly oxidizing flame, when used in burners having an air supply, designed for a gas requiring more oxygen.

The behavior of platinum when heated under the last five conditions may be explained by the hypothesis that a volatile oxide of platinum is formed, stable at high and low temperatures, but unstable at intermediate temperatures, like the platinous chloride ( $\text{Pt Cl}_2$ ) of Troost and Hautefeuille.<sup>1</sup>

If, as is the case in the blast-flame, the compound is swept away or if, as in the porcelain furnace in the combustion tube and with the heated wire, there is no cooler part of the platinum, upon which the metallic product of the decomposition of the hypothetical oxide can settle, the platinum loses weight. If on the contrary the flame is a quiet one, as is the case when a crucible is heated in a Bunsen flame, and only a part of the metal is very strongly heated, the hypothetical oxide decomposes at once on emerging from the most strongly heated zone and the platinum is deposited on the cooler part of the crucible, producing the molecular change of the surface, without gain or loss of weight, noticed by Erdmann and Crookes.

It is hoped to continue this work in this laboratory, to examine the deposit, to test the behavior of purer platinum, to try to isolate the hypothetical oxide and to fix, if possible, the conditions under which commercial platinum may be heated to whiteness without loss.

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NEW YORK UNIVERSITY, June, 1900.

## THE PRECIPITATION OF THE SULPHIDES OF NICKEL AND COBALT IN AN ALKALINE TARTRATE SOLUTION, TOGETHER WITH AN INVESTIGATION INTO THE NATURE OF CERTAIN TARTRATES OF THESE METALS.

BY O. F. TOWER.

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### INTRODUCTION.

VILLIERS<sup>2</sup> recommended some time ago a method for the qualitative separation of nickel and cobalt based on the action of hydrogen sulphide on an alkaline solution of the tartrates

<sup>1</sup> *Compt. rend.*, 84, 946 (1877).

<sup>2</sup> *Ibid.*, 119, 1263, and 120, 46 (1894-95).

of these metals. This method as commonly carried out may be stated as follows: The solution of the sulphides of nickel and cobalt in aqua regia is evaporated to expel chlorine, and after suitable dilution sufficient tartaric acid is added to prevent precipitation by sodium hydroxide. This last reagent is then added until the solution is strongly alkaline, and hydrogen sulphide run in to saturation. Cobalt sulphide is precipitated, while nickel sulphide remains in solution, imparting to the solution a dark color. When nickel is present only in very small quantities the color is brown; with larger quantities it is a jet black.

The failure of this method to give good results in the hands of students, has led to a critical investigation of it, the results of which are given in the following pages. In order to be able to approach this subject intelligently this account will be preceded by an account of an investigation into the nature of some tartrate solutions of nickel and cobalt, together with a description of any such tartrates which it has been found possible to isolate.

All substances before being analyzed were dried in an air-bath at 120°.

Nickel and cobalt were always determined electrolytically following in most respects the method of Fresenius and Bergmann,<sup>1</sup> which may be outlined as follows: To the solution containing nickel or cobalt, which is free from chlorides, are added 100 cc. ammonia solution (sp. gr. 0.96) and 10 cc. of a solution of ammonium sulphate (305 grams to liter). A current from two storage battery cells (3.2 volts, 0.48 ampere) was passed through the solution for from four to five hours. This length of time was found to be sufficient to effect complete precipitation of the metal (quantities not exceeding 0.1100 gram), provided tartrates were absent. It was necessary, however, to determine these metals frequently in the presence of tartrates. In such cases the amount of metal deposited at the end of four or five hours was weighed, removed from the electrode, and the apparatus then reconnected and left running all night. The results were then very satisfactory.

Potassium was determined as sulphate. After removing the nickel either by precipitation as sulphide or by electrolysis, tar-

<sup>1</sup> *Ztschr. anal. Chem.*, 19, 314 (1880).

taric acid was destroyed by gentle ignition, and the potassium then converted into sulphate by heating with ammonium sulphate.

#### TARTRATES OF NICKEL.

The effect of tartaric acid in preventing the precipitation of the hydroxides of nickel and cobalt has been known since the time of Rose,<sup>1</sup> and since then has been frequently discussed. The literature on the preparation of well-defined tartrates of these metals is, however, rather meagre.

That nickel tartrate cannot be precipitated from solutions of nickel salts is well known. Werther<sup>2</sup> prepared it by saturating a boiling solution of tartaric acid with freshly precipitated nickel hydroxide. The substance was thrown down as a pale green powder practically insoluble in hot or cold water, but soluble in warm alkalis. This has been essentially confirmed. The precipitate is apparently amorphous, although Werther considered it crystalline. The filtrate is still colored green, showing that precipitation is incomplete, but what is precipitated is extremely insoluble in water. The substance washed and dried at 120° yielded 28.44 per cent. nickel. The theoretical percentage of nickel in  $\text{NiC}_4\text{H}_4\text{O}_6$  is 28.39. This substance dissolves readily in alkalis, only when they are present in large excess. To effect solution, considerably more potassium hydroxide is required than a quantity equivalent to the nickel tartrate; that is, more than two molecules potassium hydroxide to one nickel tartrate, and the action is greatly accelerated by heating. The behavior of this nickel tartrate toward atmospheric moisture is worthy of remark. The precipitated powder dried at 50° still contains moisture. In this condition, however, it neither deliquesces nor effloresces, the moisture content remaining constant. On the other hand no definite hydrate seems to exist, for different samples on drying at 120° were found to contain different percentages of residual water. Furthermore, the water-free substance is not in the least hygroscopic. When exposed under a bell-jar to an atmosphere saturated with moisture, it does not gain in weight more than a milligram or two in several weeks. Nickel tartrate can be made

<sup>1</sup> Gilbert's *Annalen*, 73, 74, foot-note (1823).

<sup>2</sup> *J. prakt. Chem.*, 32, 400 (1844).

equally well by treating a hot solution of tartaric acid with nickel carbonate.

Fresenius<sup>1</sup> prepared a hydrated racemate of nickel from nickel acetate and racemic acid. It resembles nickel tartrate in some of its characteristics but was not further investigated.

If freshly precipitated nickel hydroxide is treated with cold dilute tartaric acid, the nickel hydroxide dissolves, imparting to the solution a green color, probably due to the formation of nickel tartrate. On warming this solution the light green powder mentioned above precipitates. To determine the molecular size of the substance in solution, a solution was prepared by treating an excess of nickel hydroxide with a known quantity of tartaric acid, and then finding the freezing-point of the resulting solution. The reaction between nickel hydroxide and tartaric acid is very slow, so that after five days' standing free tartaric acid was still present in sufficient quantity to redden blue litmus paper, 2 or 3 milligrams of the acid being uncombined. This was not sufficient to influence materially the results which follow. The apparatus employed for the freezing-point determinations was Beckmann's improved form,<sup>2</sup> and is particularly designed to exclude moisture from the solution during the process. This is accomplished by operating the stirrer by means of an electromagnet, thereby obviating the necessity of having a hole through the stopper for the stirring shaft. Since aqueous solutions were used in these experiments, the exclusion of moisture made very little difference, but this form of apparatus has other advantages. It is exceedingly convenient, requiring the operator's attention only for a few minutes at the time of freezing, and besides the regularity of stirring insures greater accuracy. Individual determinations of the freezing-point of the same substance did not vary more than 0.002°. Five cells of a storage battery were used to supply power for the electromagnet. Table I gives the results with solutions of nickel tartrate prepared as indicated above. The last four are with different concentrations of the same solution. The strength of such solutions was always determined by precipitating the nickel in an aliquot portion by electrolysis.

<sup>1</sup> *Ann. Chem.* (Liebig), 41, 23 (1842).

<sup>2</sup> *Ztschr. phys. Chem.*, 21, 239 (1896).

TABLE I.

Amount $\text{NiC}_4\text{H}_4\text{O}_6$ in 100 cc. solution. Grams.	Depression.	Apparent Molecular weight.
1.8795	0.139°	260
1.7205	0.121°	273
0.8602	0.081°	202
0.4301	0.042°	193
0.2150	0.025°	163

Molecular weight of  $\text{NiC}_4\text{H}_4\text{O}_6 = 206.8$ .

In the case of the more concentrated solutions these results show the molecular weight calculated from the lowering of the freezing-point to be higher than that calculated from the formula. One would expect, however, the reverse, because of dissociation in aqueous solution. By the freezing-point method Kahlenberg has shown the apparent molecular weight of potassium tartrate in solutions of moderate strength to be about one-half that calculated from the formula,  $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ .<sup>1</sup> These facts lead to the conclusion that nickel tartrate exists in fairly concentrated solutions largely in the form of double molecules.

Determinations of the electrical conductivity of these solutions show abnormal results also. In Table 2,  $m$  is the fraction of a gram-equivalent ( $\frac{1}{2}\text{NiC}_4\text{H}_4\text{O}_6$ ) in a liter;  $L$  is the equivalent conductivity expressed in reciprocal ohms.<sup>2</sup>

TABLE 2.

Temperature 18°.		Temperature 25°.	
Nickel tartrate.		Magnesium tartrate. <sup>3</sup>	
$m$ .	$L$ .	$m$ .	$L$ .
0.1664	8.29	0.03125	54.9
0.0832	9.34	0.0156	64.1
0.0416	10.8	0.0078	74.0
0.0208	18.7	0.0039	82.6
0.0104	26.5	0.0020	90.1
0.0052	36.8	0.0010	95.9
0.0026	48.8	.....	....
0.0013	63.6	.....	....

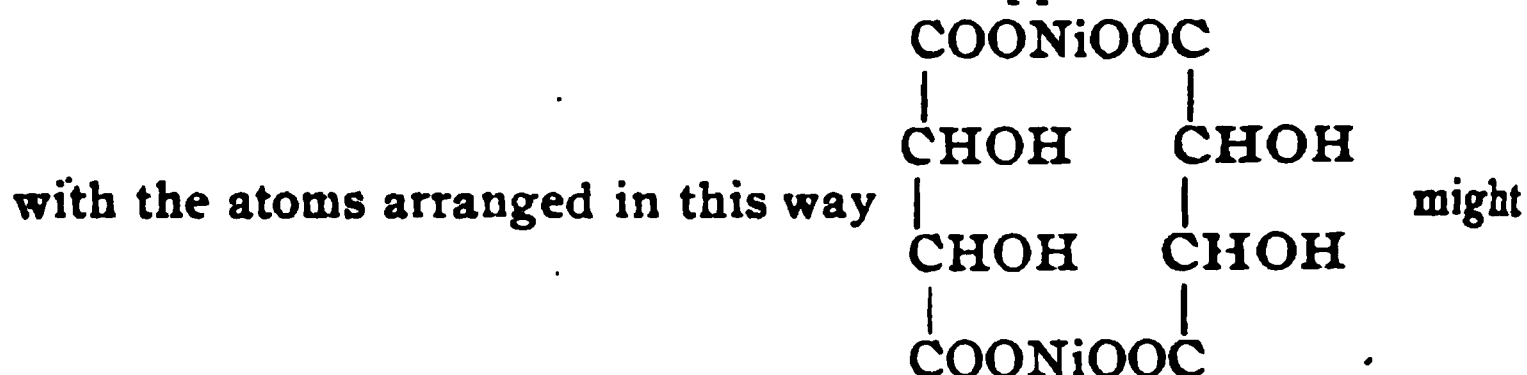
The values of the conductivity of nickel tartrate are exceptionally small, as will be seen by comparing them with the values for magnesium tartrate, which illustrate normal conduc-

<sup>1</sup> *Ztschr. phys. Chem.*, 17, 585 (1895).

<sup>2</sup> These units are those proposed by Kohlrausch, and fully described in "Leitvermögen der Elektrolyte," by Kohlrausch and Holborn.

<sup>3</sup> Determinations by Walden, *Ztschr. phys. Chem.*, 1, 537 (1887), recalculated by Kohlrausch and Holborn.

tivities of tartrates of this class. The different behavior of nickel tartrate can only be ascribed to a peculiar constitution of the salt itself. It seems reasonable to suppose that a substance



well suffer less dissociation than a normal tartrate. Dissociation in concentrated solutions would probably be of the nature,  $\text{Ni}^{++}$  and  $\text{C}_4\text{H}_4\text{O}_6\text{NiC}_4\text{H}_4\text{O}_6^-$ . On dilution this anion itself would gradually be decomposed, so that the conductivity would not advance with the same regularity as it does in the case of simple binary electrolytes. In Table 2, the results with nickel tartrate show such behavior, as is seen by comparison with the value for magnesium tartrate. Such a formula as the above will also explain very satisfactorily the results obtained from the freezing-point method. Measurements of the electromotive forces with solutions of this kind will not be given, until the facts relating to some other tartrates of nickel have been discussed.

Fabian<sup>1</sup> prepared potassium nickel tartrate by allowing cream of tartar to act on nickel carbonate at a temperature of about 50°. On evaporating the solution obtained over sulphuric acid a greenish substance was deposited, which effloresced on exposure to air and was soluble in water. After drying this substance at 110° and analyzing, he obtained the following results :

	Found. Per cent.	Theory for $\text{NiK}_2\text{C}_4\text{H}_4\text{O}_6$ Per cent.
NiO .....	16.8	17.3
K <sub>2</sub> O .....	20.9	21.7

This work has been repeated with essentially the same results. Cream of tartar was allowed to stand in contact with an excess of nickel carbonate at about 40° for some time. The green solution was filtered off, and left to evaporate over sulphuric acid. No definite crystals were obtained, neither by evaporating rapidly in a partial vacuum nor slowly in the air with a string.

The residue was invariably of a scaly appearance possessing

<sup>1</sup> *Ann. Chem. (Liebig)*, 103, 248 (1857).



a very light green color. The results of the analysis of this substance are :

	Found. Per cent.	Theory for $K_2NiC_8H_8O_{12}$ . Per cent.
K.....	18.21	18.06
Ni .....	13.38	13.55

According to Fabian, on boiling a solution of this substance a gelatinous mass separates out, which cannot be washed completely free from alkali. This has been found to be true, the precipitate being rather flocculent and of a very light green color. If, however, a solution of potassium nickel tartrate is digested for some time at about  $75^\circ$ , a light green pulverulent precipitate can be obtained, which was supposed to be a basic tartrate of nickel. After washing it thoroughly and drying at  $120^\circ$ , analysis proved it to be identical with the insoluble nickel tartrate already described, a sample yielding 28.25 per cent. nickel. On long standing this decomposition takes place gradually at lower temperatures. It is, therefore, necessary to exercise care in the preparation of potassium nickel tartrate, for, if tartaric acid is digested for a long time with nickel carbonate, some of the potassium nickel tartrate formed is apt to decompose in this manner :

Insoluble form.



When the solution is filtered, the potassium tartrate passes through with the potassium nickel tartrate, and remains mixed with it on evaporation. This is revealed by the percentage of potassium being too high and that of nickel too low to correspond to the formula  $K_2NiC_8H_8O_{12}$ .

Determinations of the molecular weight of this substance were made by means of the freezing-point method. For this purpose different solutions were employed,—some prepared as above described, some by dissolving the solid substance in water, and others by dissolving nickel hydroxide in the proper amount of tartaric acid and adding that quantity of potassium hydroxide just sufficient to form  $K_2NiC_8H_8O_{12}$ . The results follow :

TABLE 3.

	Amount $K_2NiC_8H_8O_{12}$ in 100 cc. solution. Grams.	Depres- sion.	Apparent molecular weight.
Solution prepared direct from	3.764	0.434 <sup>C</sup>	162
$NiCO_3$ and $HKC_4H_4O_6$ .....	1.882	0.255	140
	0.941	0.170	105
Solid substance dissolved in	3.752	0.430	165
water.....	1.876	0.253	140
Solution prepared from $Ni(OH)_2$ ,	3.295	0.419	153
$H_2C_4H_4O_6$ and $KOH$ .....	1.6475	0.246	128
	0.8238	0.139	112
	0.4119	0.079	98

Molecular weight of  $K_2NiC_8H_8O_{12} = 433$ .

It is essential to know something about the dissociation of this substance before one can judge intelligently of its true molecular size. To throw light on this subject the electrical conductivity of a solution of potassium nickel tartrate was measured. The equivalent conductivity is given on the basis of one potassium atom ( $\frac{1}{2}$  molecule  $K_2NiC_8H_8O_{12}$  in a liter).

TABLE 4.

Temperature 18°. Potassium nickel tartrate.		Temperature 25°. Sodium tartrate. <sup>1</sup>	
m.	L.	m.	L.
0.1522	74.6	.....	.....
0.0761	84.3	.....	.....
0.0381	94.2	0.03125	87.1
0.0190	101	0.0156	93.2
0.0095	114	0.0078	98.2
0.0048	124	0.0039	102.1

The conductivity of the double tartrate is increasing with the dilution much faster than that of the sodium tartrate. This is undoubtedly due to the dissociation of potassium nickel tartrate mostly into  $K^+$  ions and  $NiC_8H_8O_{12}^-$  ions in the more concentrated solutions. On dilution, however, the nickel also begins to dissociate from the complex anion, thus causing the rapid increase in the conductivity. For corresponding concentrations the conductivity of the double tartrate always exceeds that of the sodium tartrate.

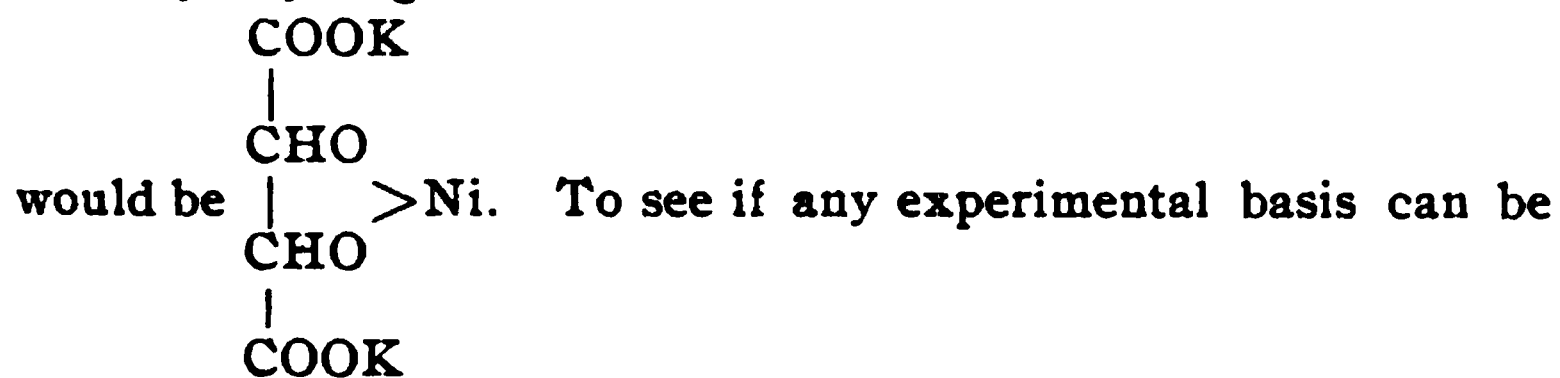
Kahlenberg,<sup>2</sup> in his article on complex tartrates of lead and

<sup>1</sup> The conductivity of sodium tartrate is given for comparison. The results are those of Bredig, *Ztschr. phys. Chem.*, 13, 191 (1894), recalculated by Kohlrausch and Holborn.

<sup>2</sup> *Ztschr. phys. Chem.*, 17, 577 (1895).

copper, found that these substances were probably dissociated sufficiently, so that the apparent molecular weight was about one half the true molecular weight. The solutions of potassium nickel tartrate used here were, however, a little more dilute than Kahlenberg's solutions; besides the substances are somewhat different in nature. Table 3 shows the apparent molecular weight to be only a little more than  $\frac{1}{2}$  of the molecular weight of  $K_2NiC_4H_4O_{12}$ . This may be accounted for on two hypotheses; either the substance is in large part dissociated into  $K^+$ ,  $K^+$  and  $NiC_4H_4O_{12}^-$  ions as was indicated in connection with the conductivity measurements, or there exist separately in the solution potassium tartrate and nickel tartrate, the former dissociated, the latter, however, not. The evidence seems to favor the former of these hypotheses. For, if the second were correct, one would expect the deposit left on evaporation of the solution not to have a uniform composition. But the deposit on the side of the dish was of the same composition as that on the bottom. Furthermore, washing the deposit slightly with water had no effect on its composition. If the substance had been a mixture of potassium tartrate and nickel tartrate, this treatment would very likely dissolve more of the former salt than of the latter.

The fact that the addition of tartaric acid to solutions of nickel salts prevents the precipitation of nickel hydroxide is usually explained by the supposition that in such cases the nickel replaces the hydrogen atoms of the alcoholic hydroxyls of the tartaric acid, while the potassium takes the place of the two carboxyl hydrogen atoms. The formula of such a substance



found for this view, solutions of nickel tartrate, to which potassium hydroxide had been added, were investigated by the usual physico-chemical methods.

The freezing-point method was first employed in order to observe the effect on the size of the molecule of successive

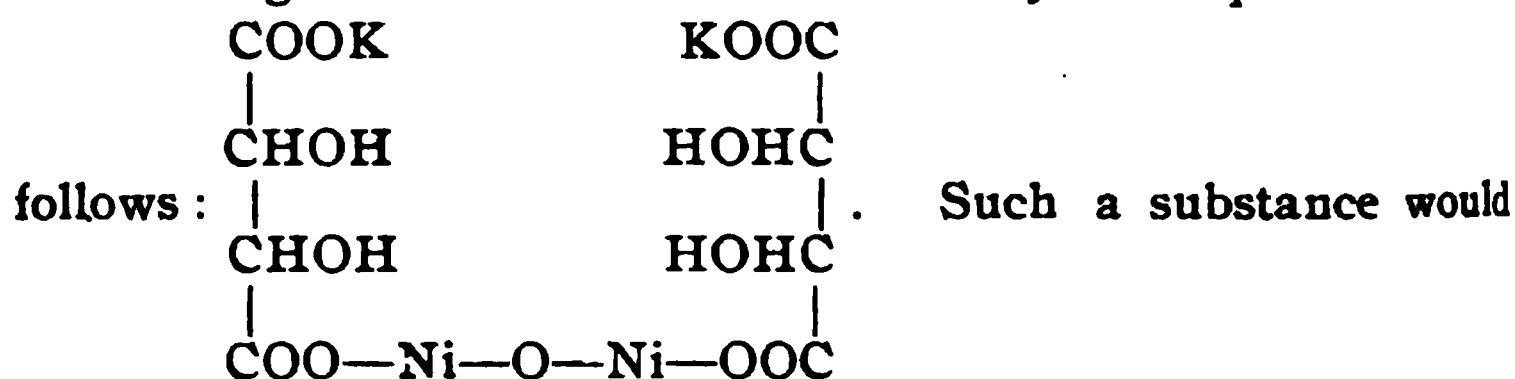
additions of potassium hydroxide<sup>1</sup> to a solution of nickel tartrate.

TABLE 5.

Solution containing 1.8795 grams nickel tartrate in 100 cc.

Expt. No.	KOH added to above solution. Gram.	Depression.	Remarks.
1	0.0000	0.139°	Reaction acid.
2	0.1226	0.180	Reaction alkaline.
3	0.3270	0.187	
4	0.5314	0.134	
5	0.7358	0.180	Solution jelly-like.
6	0.8175	0.156	
7	1.311	0.233	

In Experiment 7, the quantity of potassium hydroxide is just sufficient to form, with the nickel tartrate,  $K_2NiC_4H_4O_6$ . In the fourth the depression is a minimum, and here the amount of potassium hydroxide added is nearly one half that added in the seventh, or the ratio is about one molecule potassium hydroxide to one nickel tartrate. If the molecular weight is calculated from the depression,  $0.134^\circ$ , on the basis of  $NiKC_4H_4O_6$  existing in solution, 299 is obtained. The molecular weight according to the above formula is in round numbers 245. This case is almost exactly parallel to the results obtained by Kahlenberg<sup>2</sup> with certain alkaline tartrate solutions of lead and copper. So undoubtedly the molecular size of the substance here is about twice that represented by the formula  $NiKC_4H_4O_6$ , and following Kahlenberg the molecular structure may be represented as



hardly be expected to dissociate so as to yield nickel ions. The evidence for such a molecular structure would, therefore, be increased, if it could be shown that no nickel ions exist in the solution.

For this purpose measurements were made of the electromotive force generated by an element with nickel electrodes, one

<sup>1</sup> Sodium hydroxide was also employed, but since the results are similar, only those with potassium hydroxide are given.

<sup>2</sup> *Loc. cit.*

electrode being surrounded by a solution of a nickel salt of known concentration and the other surrounded by the solution in question. The electromotive force of such an element is expressed by the formula,

$$\pi = \frac{RT}{nE_0} \ln \frac{c_1}{c_2},$$

where the letters indicate the usual quantities,  $c_1$  and  $c_2$  being the concentration of the nickel ions in the two solutions. Evaluating the equation for  $R = 8.311$  electrical units,  $T = 291$  ( $18^\circ$  C.),  $n$ , the valence of nickel  $= 2$ ,  $E_0 = 96,540$  coulombs, and reducing to Briggs' system of logarithms, one obtains,

$$\pi = 0.02881 \log \frac{c_1}{c_2}.$$

Measurements were made according to the Poggendorf-Ostwald method with a Lippmann capillary electrometer. The nickel solution of constant concentration was in every case a solution of nickel nitrate containing 0.1 gram-molecule in a liter. The electrodes were made by covering platinum electrodes with nickel by electrolysis. These electrodes were tested by connecting them with an electrometer, when they were dipping into the same solution of nickel nitrate. Under these conditions the electrometer reading should be zero. Few electrodes, however, could be found which would fulfil this condition. Those chosen showed potential differences of not more than 0.003 volt. Measurements were made first of the electromotive forces between the standard solution and solutions of nickel nitrate containing 0.05 and 0.01 gram-molecule in a liter, respectively, and afterwards with the solutions of nickel tartrate under consideration. In each case the electrodes were reversed and the potential difference measured again. The averages of the two readings so obtained are given in Table 6.

TABLE 6.  
Temperature  $18^\circ$ .

No.	Between 0.1 mol. $\text{Ni}(\text{NO}_3)_2$ and	$\pi$ observed. Volt.	$\pi$ calculated. Volt.
1	0.05 mol. $\text{Ni}(\text{NO}_3)_2$	0.010	0.0087
2	0.01 " "	0.032	0.0288
3	0.0208 " $(\text{NiC}_4\text{H}_4\text{O}_6)_2$	0.048	.....
4	0.0761 " $\text{NiK}_3\text{C}_3\text{H}_5\text{O}_{12}$	0.075	.....
5	0.0572 " $\text{KC}_4\text{H}_4\text{O}_6\text{NiONiO}_6\text{H}_4\text{C}_4\text{K}_2$	0.210	.....
6	0.0748 " $\text{K}_2\text{NiC}_4\text{H}_2\text{O}_6$	0.236	.....

Where the concentration of the nickel ions was known the electromotive force has been calculated from the formula. The agreement is seen to be fairly good. Nos. 3 and 4 are measurements with the solutions already mentioned of nickel tartrate and potassium nickel tartrate, respectively. The potential differences show that the concentration of the nickel ions in these solutions is somewhat less than in a 0.01 mol. solution of nickel nitrate. Fewer nickel ions are present in the potassium nickel tartrate solution than in the solution of nickel tartrate, which was to be expected, for the same reason that the replaceable hydrogen atom of an acid salt is only very slightly dissociated.<sup>1</sup>

To find the concentration of the nickel ions in solution 5, which is the one formed by adding to 100 cc. of a solution containing 18.795 grams of nickel tartrate, 0.5314 gram of potassium hydroxide,<sup>2</sup> 0.210 is substituted for  $\pi$  in the formula and  $c_1$  is made equal to  $0.1 \times 0.8$ , for 0.1 mol. nickel nitrate is about 80 per cent. dissociated. From this the value of  $c_1$  is found to be  $10^{-8.386}$ . This shows that, relatively speaking, no nickel ions are in the solution, which is corroborative evidence of the existence of the molecular structure ascribed to this substance on page 510.

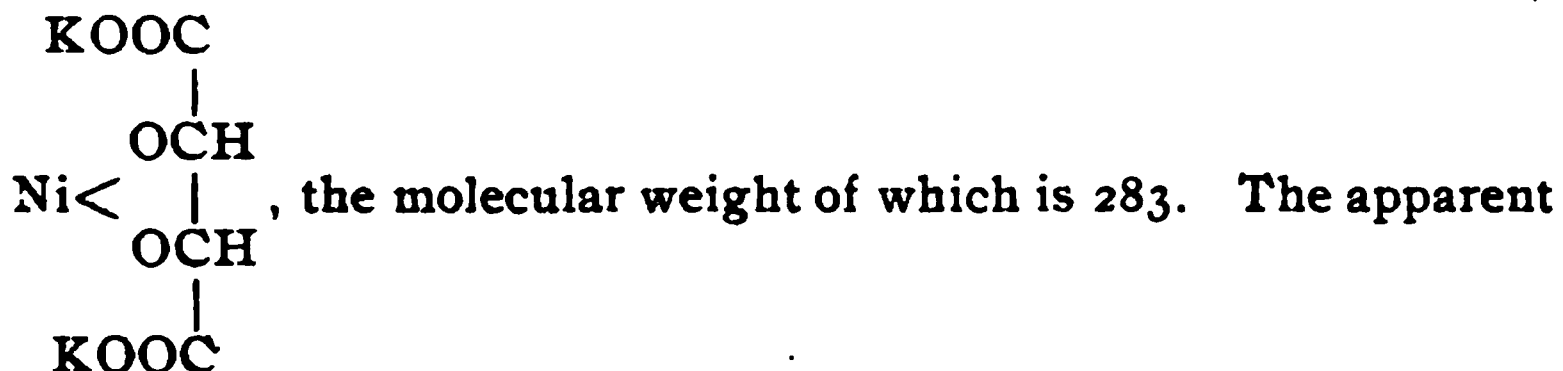
Referring to Table 5, it will be noticed that the depression gradually increases with the addition of potassium hydroxide from the fourth experiment to the seventh, except in No. 5. In this case the contents of the tube were viscous having the consistency of thin jelly, which interfered materially with the determination. This gelatinous mass completely dissolved on addition of more potassium hydroxide. The appearance of this substance is peculiar. The green liquid simply solidifies to a transparent mass without any change in appearance. On reversing the tube containing the substance it is found to be solid or viscous according to the amount of water present, and this is the only evidence of a change. On standing for a length of time it gradually becomes opaque. Several years ago this phenomenon was observed by Professor Bradley, of Middletown, who called my attention to it at that time. He obtained it by adding first tartaric acid to a solution of nickel sulphate and then adding a solution of potassium hydroxide drop by drop

<sup>1</sup> For the discussion of this, see Ostwald: *Ztschr. phys. Chem.*, 9, 553 (1892).

<sup>2</sup> See Table 5.

until the mass gelatinized. As can be seen from Table 5, it is formed when about one molecule of nickel tartrate is treated with one molecule of potassium hydroxide. It was shown just before the solution gelatinized (experiment 4, Table 5), that from the depression of the freezing-point and other considerations the molecule probably is  $\text{KC}_4\text{H}_4\text{O}_6\text{NiONiO}_6\text{H}_4\text{C}_4\text{K}$ . It is, therefore, possible that this gelatinous mass is a hydrated form of that substance. Heating almost to the boiling-point completely dissolves it.<sup>1</sup>

To return to the effect on the depression of the freezing-point of adding potassium hydroxide, as seen in Table 5 from Experiment 4 on. Leaving out of consideration No. 5, where the solution was viscous, the increase in the depression from  $0.134^\circ$  to  $0.156^\circ$  and in the last case to  $0.233^\circ$  is by no means sufficient to be equal to the entire effect of the potassium hydroxide added, if it existed as such in the solution. 0.4935 gram more of potassium hydroxide was added in Experiment No. 7 than in No. 6. This quantity of potassium hydroxide should give normally a depression of  $0.121^\circ$ ,<sup>2</sup> but the difference between  $0.233^\circ$  and  $0.156^\circ$  is only  $0.077^\circ$ . In No. 7 the proportion of potassium hydroxide to nickel tartrate is two molecules of the former to one of the latter, or in the proper ratio to form



<sup>1</sup> Since writing this, Prof. Bradley has kindly allowed me to look over an unpublished manuscript by himself and F. A. Johnston on "A Tartrate of Sodium and Nickel," which treats of the formation, conduct, and gives some results of the analysis of this gelatinous substance. It was prepared from nickel sulphate, tartaric acid, and sodium hydroxide. It was isolated by stirring it up in alcohol, filtering and then washing with an equal volume of alcohol and water. When so treated the gelatine frequently remains transparent for a long time. It was found difficult to dry it to constant weight over sulphuric acid, for it is exceedingly hygroscopic. Preliminary analysis of the substance after drying over sulphuric acid showed: water, 7.04 per cent.; sodium, 6.30 per cent.; nickel, 21.04 per cent. We obtain by calculation from the above formula plus 2 molecules of water,  $\text{Na}_2\text{Ni}_2\text{C}_4\text{H}_4\text{O}_{12} + 2\text{H}_2\text{O}$ : water, 7.04 per cent.; sodium, 9.00 per cent.; nickel, 23.95 per cent. The most marked difference between these results and the results of the analysis is in the percentage of sodium. This may be accounted for from the fact that the gelatine is strongly alkaline and that washing removes some of this alkali, so that the residue may not have a constant composition. However, it is not asserted that the above formula represents the composition of the substance, for more analyses are needed in which the amount of tartaric acid is also determined, before the differences in the above results are explained and a suitable formula established.

<sup>2</sup> Calculated from the constant for potassium hydroxide reported by Raoult, *Ann. chim. phys.* (5), 28, 137 (1883).

molecular weight calculated from the depression, 0.233 is 185, which is a little more than half that calculated from the formula. Since such a substance would probably be dissociated in aqueous solution about as much as potassium tartrate,<sup>1</sup> it is very likely that a substance of the above formula does really exist in the solution. Nickel ions would not be expected to be present in any quantity in a solution of such a substance. The potential difference found between this solution and 0.1 mol. nickel nitrate is 0.256 volt (No. 6, Table 6). This shows that the concentration of the nickel ions is even less than in the preceding solution (No. 5), where the concentration of these ions was found to be  $10^{-8.386}$ . What has, therefore, probably taken place on the addition of potassium hydroxide from solution 4 to solution 7, Table 5, is that, although the potassium hydroxide is continually being removed from the field of action as such, the molecular structure of the substance in solution is undergoing a change; that is, the complex molecule,  $\text{KC}_4\text{H}_4\text{O}_6\text{NiONiO}_6\text{H}_4\text{C}_4\text{K}$ , is breaking up into the smaller molecule,  $\text{K}_2\text{NiC}_4\text{H}_4\text{O}_6$ ; the number of molecules is, consequently, on the whole increased, and the depression of the freezing-point becomes greater.

#### TARTRATES OF COBALT.

Very little literature of a definite nature could be found on this subject. A tartrate of cobalt and a double tartrate of potassium and cobalt are mentioned in the following dictionaries of chemistry: Fehling's, Vol. 9 (1864); Watts', Vol. 5 (1868); Wurtz's, Vol. 3 (1878). Nearly all the early journals and such periodicals as Berzelius' *Jahresbericht*, Liebig and Kopp's *Jahresbericht*, the *Pharmaceutisches Centralblatt*, &c., were thoroughly searched, but no reference was found to the original articles describing these salts. Such works as Ladenburg's Dictionary, edition 1894, and Beilstein's, third edition, mention no such substances. It is, therefore, to be inferred that the original article contained nothing very definite. Fresenius' prepared certain racemates of cobalt, but gives no analyses.

Cobalt tartrate can be made in the same manner as nickel tartrate, by saturating hot tartaric acid with cobalt hydroxide

<sup>1</sup> See Kahlenberg, *loc. cit.*

<sup>2</sup> *Ann. Chem.* (Liebig), 41, 22 (1842).



or carbonate. It is thrown down as a pale pink powder practically insoluble in hot or cold water, and possessing in general the other properties of nickel tartrate. A sample of this dried at  $120^{\circ}$  gave 28.32 per cent. cobalt (theory, 28.49 per cent.).

When cobalt hydroxide is treated in the cold with tartaric acid it dissolves to a certain extent a pink solution resulting, which, on standing, deposits reddish pink crystalline scales of cobalt tartrate. This crystalline substance differs from the cobalt tartrate just described by being somewhat soluble in water. It is impossible to obtain as concentrated solutions of cobalt tartrate as of nickel tartrate, for the reason just mentioned, that some of the salt crystallizes out. With, however, as strong a solution as could be obtained the following determinations were made of the depression of the freezing-point.

TABLE 7.

Amount $\text{CoC}_4\text{H}_4\text{O}_6$ in 100 cc. solution. Gram.	Depression.	Apparent molecular weight.
0.6505	0.059 <sup>c</sup>	207
0.3252	0.036	170
0.1626	0.021	146

Molecular weight of  $\text{CoC}_4\text{H}_4\text{O}_6 = 207.1$ .

These results run about the same as those obtained with solutions of nickel tartrate of similar concentration. The apparent molecular weight, 207, is very nearly equal to the molecular weight calculated from the formula; therefore, for the reasons already mentioned, the true molecular weight of cobalt tartrate is probably twice 207.1, which means its structure would be represented by twice the above formula or  $(\text{CoC}_4\text{H}_4\text{O}_6)_2$ . Table 8 gives the results of the determination of the electrical conductivity of solutions of this substance. The units are on the basis of equivalent ( $\frac{1}{2} \text{CoC}_4\text{H}_4\text{O}_6$ ) in a liter as before.

TABLE 8.

<i>m.</i>	Temperature $18^{\circ}$ .	<i>L.</i>
0.0628		15.9
0.0314		22.1
0.0157		28.7
0.0079		37.6
0.0039		47.1
0.0020		58.4
0.0010		69.9
0.0005		82.1

These results are entirely analogous to the conductivity of nickel tartrate (Table 2). They are abnormally small and show that cobalt tartrate is only slightly dissociated, which affords additional evidence that the molecule is polymerized.

Cream tartar acts vigorously on cobalt carbonate in the presence of water, the resulting solution being colored a deep pink. When this solution is evaporated over sulphuric acid, reddish pink crystalline scales are deposited, very similar in appearance to the deposit from a solution of cobalt tartrate. When almost to dryness the solution assumes a pasty nature, and can be completely dried only with considerable difficulty. No salt of the formula,  $K_2CoC_8H_8O_{12}$ , could be isolated. The crystalline deposit just mentioned yielded on drying 24.53 per cent. cobalt,<sup>1</sup> and a small quantity of potassium was also found. The deposit, therefore, consists largely of cobalt tartrate, but a small amount of potassium tartrate is mixed with it. Watts' "Dictionary," and the others above cited, say that potassio-cobaltous tartrate forms large rhomboidal prisms. No such crystals could be obtained by any of the methods used here. Determinations of the freezing-point of solutions prepared from cream tartar and cobalt carbonate yielded essentially the same results as similar solutions prepared from nickel carbonate. Such results might well be in harmony with the separate existence in the solution of potassium tartrate and cobalt tartrate, so no definite knowledge of the nature of the molecules in solution could be obtained by this method. Heating this solution causes the precipitation of a light pink powder. After washing this and drying at  $120^\circ$ , 28.38 per cent. cobalt was found which showed it to be cobalt tartrate. This substance possesses all the properties and is apparently identical with the cobalt tartrate previously mentioned.<sup>2</sup> It is to be noted that the conduct of this solution on heating is somewhat different from that prepared from nickel carbonate and cream tartar, for a flocculent precipitate resulted on heating this latter to boiling.

When potassium hydroxide is added to a solution of cobalt tartrate the conduct is very similar to that when it is added to a solution of nickel tartrate. It differs, however, in this respect,

<sup>1</sup> The theoretical percentage of cobalt according to formula  $K_2CoC_8H_8O_{12}$ , is 13.61.

<sup>2</sup> That prepared by treating hot tartaric acid with cobalt hydroxide.

that when the quantities of potassium hydroxide and cobalt tartrate are in the proportion of one molecule of the former to one of the latter, instead of obtaining a gelatinous mass, a *flocculent precipitate* results, which readily dissolves on further addition of potassium hydroxide. The range of the existence of this precipitate is considerable; that is, it begins to form when the amounts of the two substances are in about the ratio of one-half molecule of potassium hydroxide to one of cobalt tartrate, and does not entirely disappear until the potassium hydroxide is present in about the ratio of  $1\frac{1}{2}$  molecules to 1 of the cobalt tartrate. This seriously interfered with following the effect on the freezing-point of successive additions of potassium hydroxide to cobalt tartrate. There is no difficulty, however, in determining the freezing-point of the solution when the potassium hydroxide is present in the ratio of two molecules of it to one of the tartrate; the results thus obtained are given in Table 9.

TABLE 9.

Amount $\text{CoC}_4\text{H}_4\text{O}_6$ in 100 cc. solution. Gram.	Amount KOH added. Gram.	Depression.
0.6505	0.0000	0.061°
0.6505	0.4530	0.106

If the molecular weight is calculated from the depression  $0.106^\circ$ , it gives 159, while according to the formula,  $\text{K}_2\text{CoC}_4\text{H}_4\text{O}_6$ , the molecular weight is 283.3. Owing to the dissociation which such a salt would suffer in aqueous solution, it is very probable that it exists here in the solution, and that it is due to its formation that cobalt hydroxide cannot be precipitated by alkalies from a solution of a cobalt salt to which tartaric acid has been added. The precipitate above referred to, formed when the amount of potassium hydroxide added to the cobalt tartrate is in the ratio of one molecule of the former to one of the latter, was filtered off and washed until the wash-water was no longer alkaline. It was then dried and the cobalt in it determined. In one sample the percentage of cobalt was 42.78 and in another 38.04. The precipitate has, therefore, no definite composition, but undoubtedly contains some cobalt hydroxide, for no conceivable tartrate of cobalt has as great a percentage of cobalt as was found.

## SOLUBLE NICKEL SULPHIDE.

It is evident that when investigating the effect of an alkaline tartrate solution in preventing the precipitation of nickel sulphide by hydrogen sulphide, it is desirable to exclude the presence of other chemical substances. Tartaric acid and sodium hydroxide were, consequently, not added to a solution of a nickel salt, as for instance the chloride, for this would produce some sodium chloride, whose influence on the precipitation with hydrogen sulphide would then be entirely unknown. Solutions of pure nickel tartrate were prepared as has already been indicated, and to this the alkali and hydrogen sulphide were then added. If it was desired to note the effect of any neutral salt, as sodium chloride, on the precipitation, such salt was added separately. All the nickel tartrate used was made from nickel nitrate, which was a preparation of Schuchardt's and was marked "*purissimum*." According to Villiers,<sup>1</sup> sodium hydroxide is more effective in holding nickel sulphide in solution than potassium hydroxide. Solutions of nickel tartrate were treated with one equivalent of sodium hydroxide,<sup>2</sup> with two equivalents of sodium hydroxide, with three equivalents, and so on. Hydrogen sulphide was run into these solutions to saturation and the solutions filtered. In the first solution nickel sulphide was precipitated and the filtrate was only slightly colored, in the second the filtrate was a decided brown, in the third it was black, but to be certain that no nickel sulphide is precipitated it is necessary to have at least five equivalents of sodium hydroxide to one of nickel tartrate. This black filtrate oxidizes with remarkable rapidity, which is shown by the continual separation of sulphur. It is apparently the sodium sulphide present, which thus suffers oxidation, but what is peculiar, is that the oxidation is more rapid than ever takes place in a solution of sodium sulphide alone. The more dilute the solution, the less marked is the oxidation. If this black alkaline solution of nickel sulphide is allowed to stand for an indefinite length of time, the nickel sulphide gradually precipitates, so that in from five to ten days the supernatant liquid has usually become clear.

<sup>1</sup> Compt. rend., 119, 1263 (1894).

<sup>2</sup> By an equivalent of sodium hydroxide is meant that quantity which bears a ratio to the nickel tartrate used of 2 molecules NaOH to 1 molecule  $\text{NiC}_4\text{H}_4\text{O}_6$ .

This settling can be greatly accelerated by the presence of a neutral salt, as sodium chloride or potassium sulphate, the time necessary for settling varying with the amount of such salt added. The presence of a large quantity of these salts before the introduction of hydrogen sulphide causes a large portion of the nickel sulphide to be precipitated.

The behavior of this black solution of nickel sulphide seemed to indicate that it is not a true solution, but colloidal in nature. To decide this several tests were applied. With a high-power microscope it was impossible to detect solid particles of any sort. The following test employed by Muthmann<sup>1</sup> was applied: It consists in treating the solution in question with a solution of gum-arabic, shaking well, and then adding alcohol to precipitate the gum. If the substance is a colloid, it is precipitated with the gum and colors it. Before applying this test it is necessary to assure one's self that alcohol will not produce a precipitate in the original solution. In this case if the alcohol did not exceed 50 per cent. of the total liquid, nothing was precipitated, so care was exercised not to add more than this amount. The gum when precipitated was colored black, and on standing a few hours the supernatant liquid became clear. The alcohol was then poured off, and the residue treated with water, which dissolved it up again, the solution being colored black as before. This is the typical behavior of a colloidal substance. Tyndall's experiment applied by Picton<sup>2</sup> to solutions of antimony and arsenic sulphides was tried with this solution. The method employed was essentially this: The liquid in question was placed in a small bottle and the bottle so supported that the rays from an arc light could be focused directly on its bottom. The light, which diffused from the side of the bottle, was examined through a nicol. A colloidal solution of arsenic sulphide was first examined to see that the apparatus gave proper results. The light was polarized, which is in harmony with the results of Picton and the later ones of Stoekl and Vanino.<sup>3</sup> The solution of nickel sulphide was then examined. On account of its dark color, it was necessary to use a very dilute solution so that the light would not be com-

<sup>1</sup> *Ber. d. chem. Ges.*, 20, 983 (1887).

<sup>2</sup> *J. Chem. Soc.*, 61, 143 (1892).

<sup>3</sup> *Ztschr. phys. Chem.*, 30, 111 (1899).

pletely absorbed. With such a dilute solution no difficulty was experienced in getting it into the bottle, before the separation of any sulphur due to oxidation could take place. The light diffused from this solution was completely polarized. Some distilled water from which the solutions were made, was then placed in the bottle and examined in the same manner. No polarization could be detected. I am greatly indebted to Mr. H. W. Woodward of the physical department of this university for very efficient aid in these optical investigations. Independent observations by him in each one of the foregoing cases confirmed mine in every particular. All these tests, therefore, seem to show that nickel sulphide exists in an alkaline tartrate solution in the colloidal state; that is, as solid particles in an extremely finely divided condition, too small to be seen with any microscope but not so small but that they reflect light.

#### COBALT SULPHIDE. \*

Cobalt sulphide was produced in a manner exactly similar to that used in preparing soluble nickel sulphide. A solution of cobalt tartrate was made alkaline with a quantity of sodium hydroxide sufficient to hold nickel sulphide in solution, and then hydrogen sulphide run in to saturation. The cobalt tartrate was prepared from chemically pure cobalt chloride of Kahlbaum's, marked "*nickel frei*." After the hydrogen sulphide had been run into the alkaline solution, it was filtered. According to Villiers, the cobalt sulphide is entirely precipitated, but in nearly every case the filtrate was colored brown. Villiers points out that by this method one can detect the presence of nickel in most preparations of cobalt supposedly free from nickel. It was, therefore, expected that the brown coloration just referred to was due to the presence of a trace of nickel. This brown filtrate was refiltered two or three times, then shaken with sodium chloride, and allowed to stand over night. In the morning a slight black sediment had deposited and the supernatant liquid was perfectly clear. The deposit was filtered off, washed and dissolved in aqua regia. After removing the excess of acid, acetic acid and potassium nitrite were added, and the mixture left twenty-four hours, at the end of which time a well-defined

yellow precipitate had appeared. This shows conclusively that the brown color of the alkaline solution was due to cobalt sulphide in solution and not nickel, for not a trace of nickel could be found in the filtrate from the nitrite precipitate. This experiment was repeated several times and nearly every time some cobalt sulphide went into solution. The presence of a moderate quantity of a neutral salt, will, however, insure complete precipitation of the cobalt sulphide.

#### CONCLUSION.

The difficulties attendant on the separation of nickel and cobalt by the method of Villiers are the following: The oxidation of the solution to which the hydrogen sulphide has been added results in the separation of so much sulphur, that if nickel is present and cobalt is not, the black solution will color the sulphur, making it very difficult to distinguish from precipitated cobalt sulphide. Furthermore, according to the process used in this separation, sodium chloride is present in the solution, and although this aids in the complete precipitation of cobalt sulphide, it may cause some nickel sulphide to be precipitated, which in the absence of cobalt sulphide might readily be mistaken for it.

The nickel sulphide in solution in an alkaline tartrate medium is in the colloidal state.

Of the different tartrates of nickel and cobalt investigated, the most interesting are the solutions of the tartrates of these metals prepared from their hydroxides and cold tartaric acid. The results of determinations of the lowering of the freezing-point and of the electrical conductivity are very exceptional for salts of this sort, and seem to point to the existence of a polymerized molecular structure.

The evidence seems to be pretty conclusive, that the cause of the non-precipitation of the hydroxides of nickel and cobalt from solutions of their tartrates, or at least that any precipitate that may form dissolves in excess of the reagent, is due to the formation of a compound in which these metals replace the hydrogen atoms of the alcoholic hydroxyl groups of tartaric acid.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA  
UNIVERSITY, No. 26.]

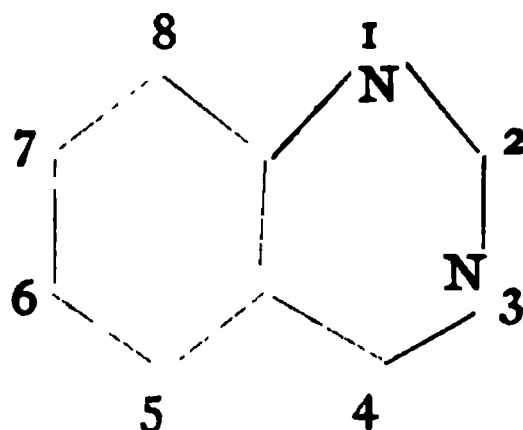
## THE DIRECT SYNTHESIS OF KETODIHYDROQUINAZOLINS FROM ORTHOAMINO ACIDS.<sup>1</sup>

BY MARSTON TAYLOR BOGERT AND AUGUST HENRY GOTTHELF.

Received June 28, 1900.

**A**S announced in our preliminary paper on this subject,<sup>2</sup> keto-dihydroquinazolins (or oxyquinazolins) can readily be obtained by the action of nitriles upon orthoamino acids under conditions of heat and pressure. The present paper is confined to a discussion of the 2-methyl-4-ketodihydroquinazolin. Many others have been prepared and studied, and will form the subjects of later communications.

For convenience, throughout this article we have called our compound a "quinazolon" although we do not intend thereby to indicate any preference for the keto form as compared with the tautomeric oxyquinazolin form. The numbering for the quinazolin nucleus is that first suggested by Paal and Busch.<sup>3</sup>



Weddige<sup>4</sup> the discoverer of this 2-methyl-4-ketodihydroquinazolin, obtained it from orthoacetaminobenzamide by fusion, by solution in alkalies with subsequent precipitation with acid, or by long boiling with water; also, by heating ethylorthoacetaminobenzoate to 160° C. with strong aqueous ammonia. Bischler and Burkart<sup>5</sup> accomplished the same result by fusing the ammonium salt of orthoacetaminobenzoic acid, while Niementowski<sup>6</sup> prepared it by heating together anthranilic acid and acetamide.

<sup>1</sup> Read before the joint meeting of the American Chemical Society and Section C of the American Association for the Advancement of Science, June 25, 1900.

<sup>2</sup> This Journal, 22, 129.

<sup>3</sup> *Ber. d. chem. Ges.*, 23, 2684.

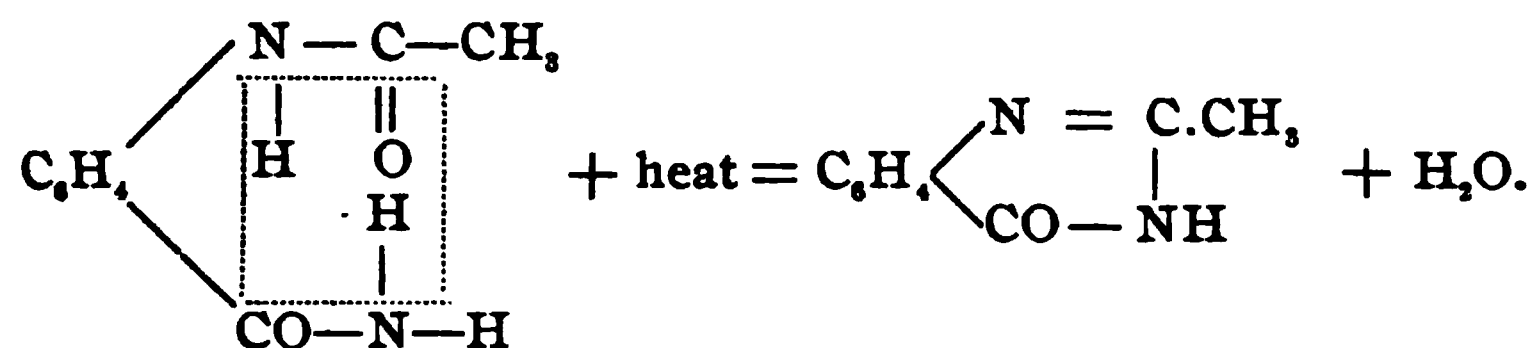
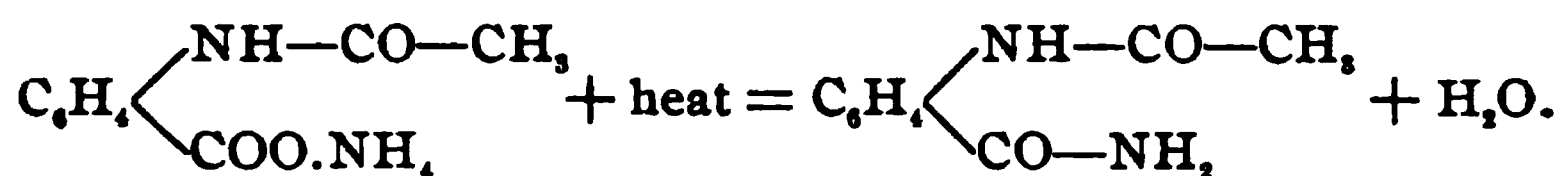
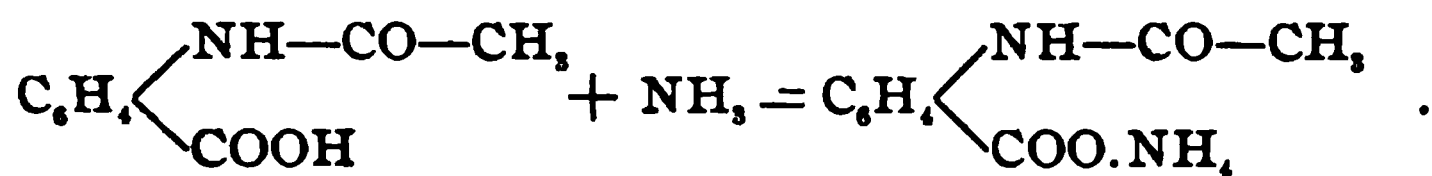
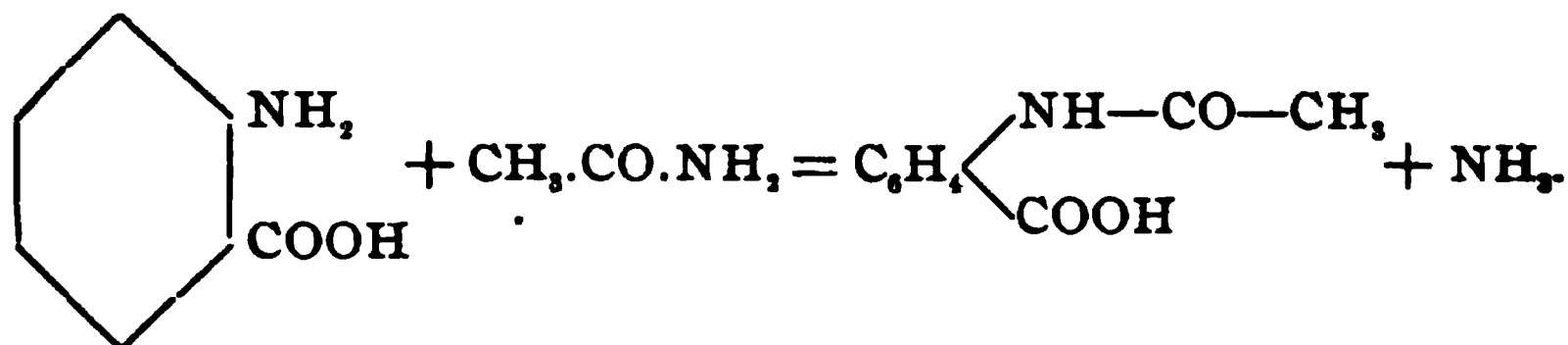
<sup>4</sup> *J. prakt. Chem.* [2], 31, 124; 36, 143.

<sup>5</sup> *Ber. d. chem. Ges.*, 26, 1350.

<sup>6</sup> *J. prakt. Chem.* [2], 51, 564.

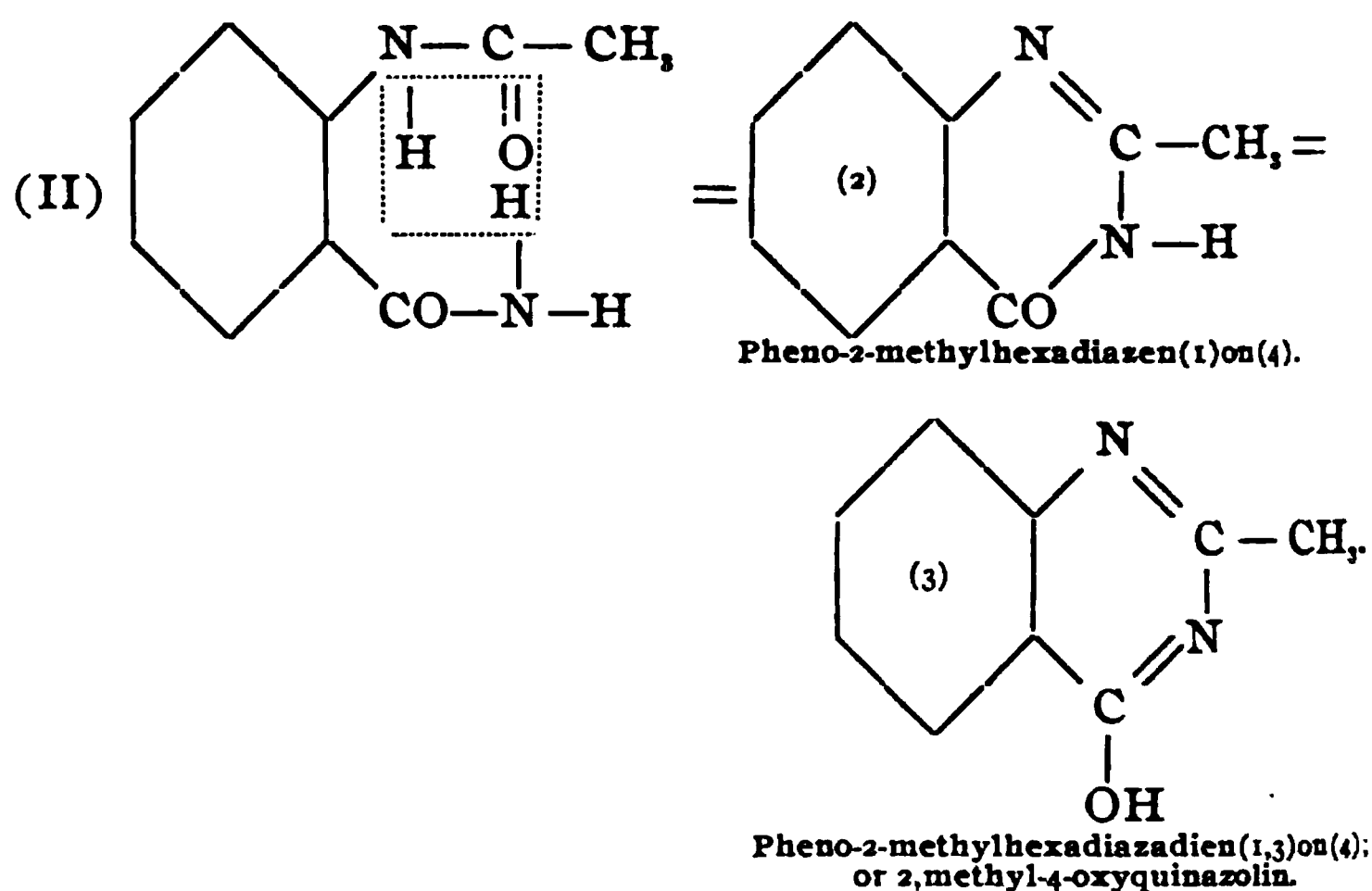
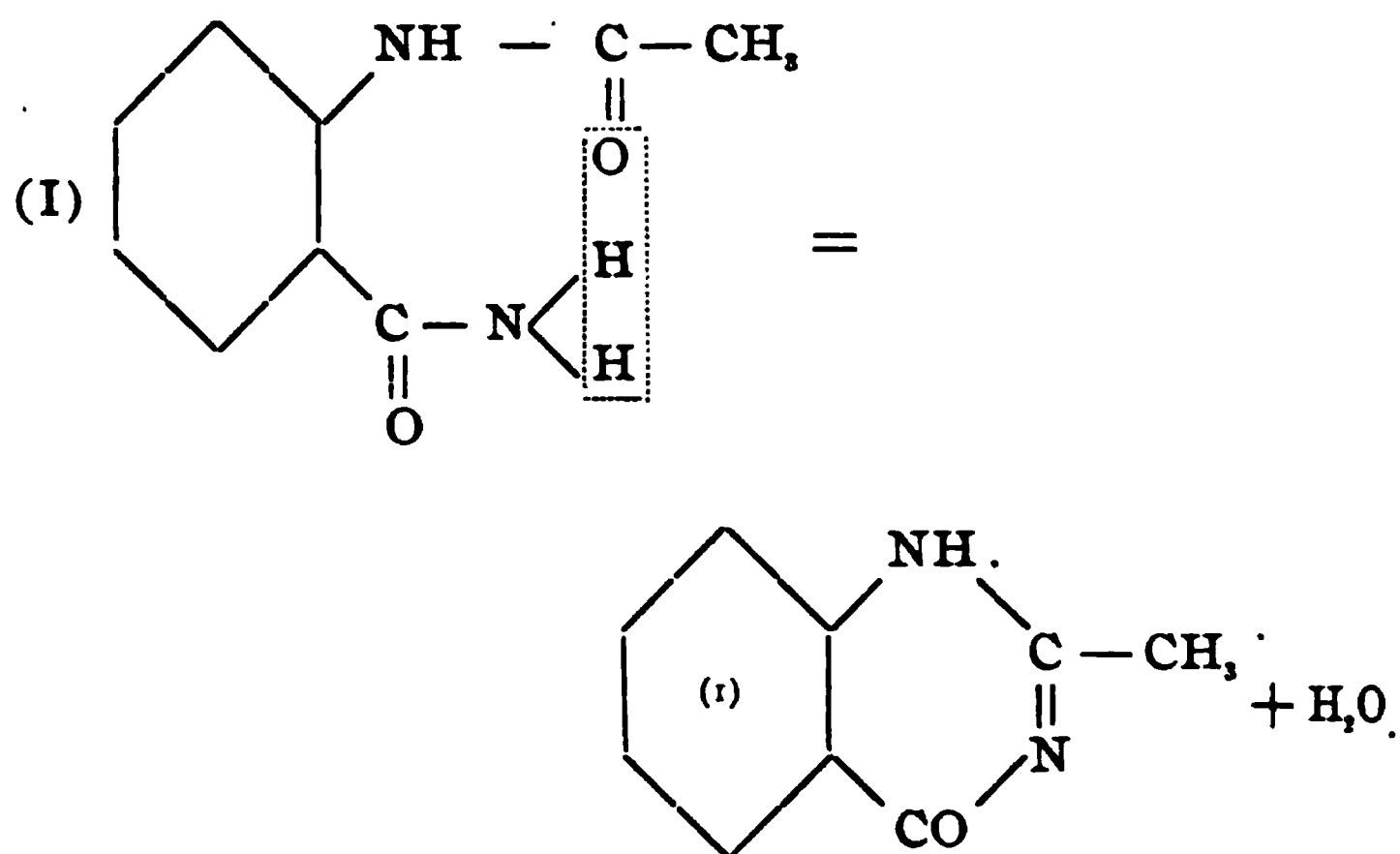


The syntheses of Weddige and Bischler are practically identical, both depending upon the formation of orthoacetaminobenzamide, from which the quinazolon results by loss of water. The course of Niementowski's synthesis is probably similar in the main, the following reactions being suggested in explanation:



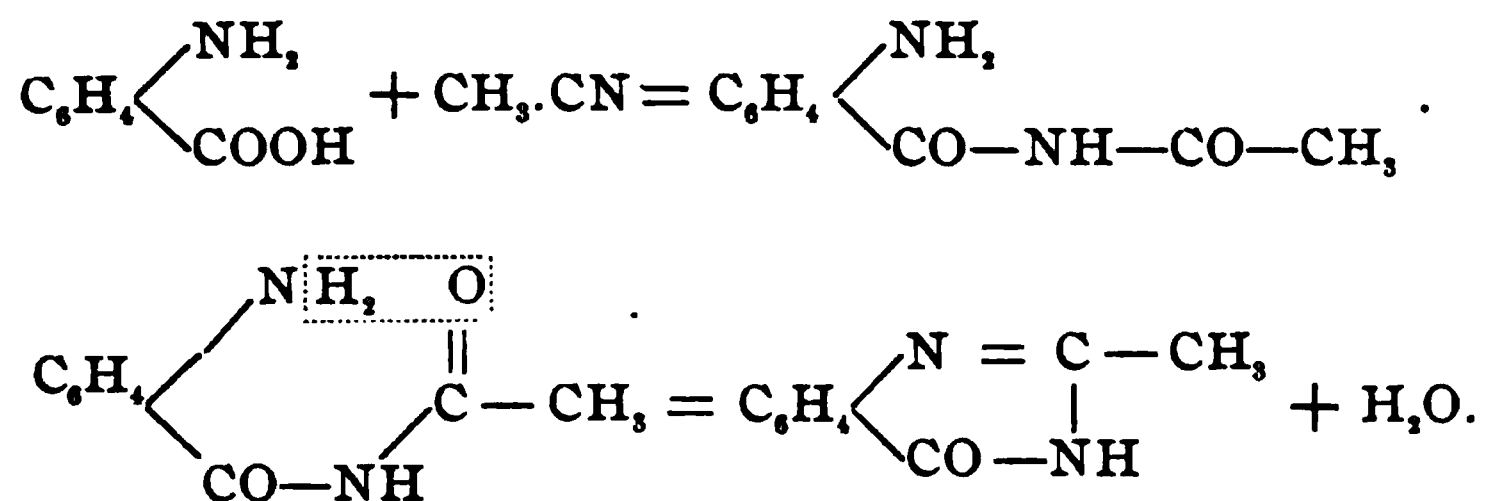
The first of these reactions seems probable when one remembers that acetanilide results from heating together aniline and acetamide, and that, with other amines, acetamide likewise yields the amide of the higher acid. The remaining reactions are then the same as in Bischler's synthesis.

In all these syntheses there is an interesting point which should not be overlooked, and that is the manner in which the water splits out in the production of the quinazolon. By an examination of the formulas, it will be seen that this may occur in two different ways, one being a lactam condensation, the other equivalent to a lactim condensation, resulting in the production of two separate and distinct isomers, as follows:

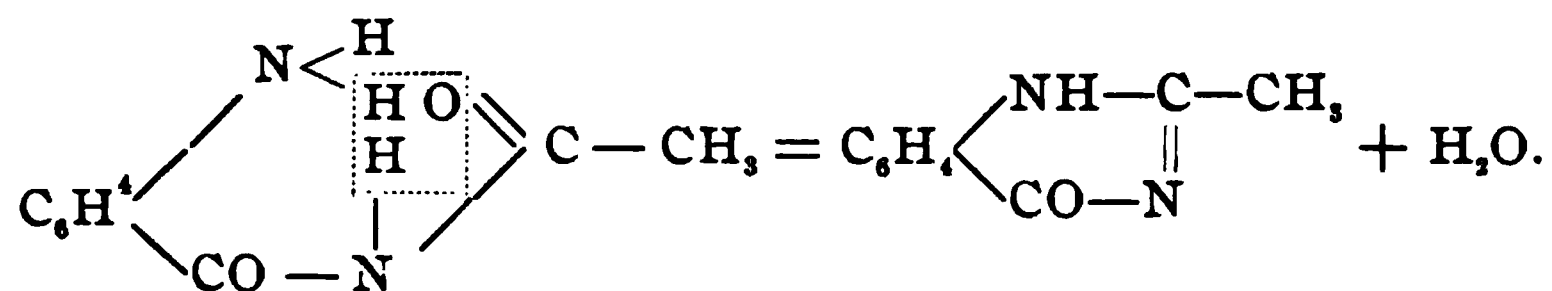


By a series of interesting reactions, Weddige proved his product to be (2) or (3), and the condensation, therefore, to have followed reaction (II). He did not, however, determine whether the compound appeared preferably in its keto or enol form, in his further studies of its properties. The products obtained by Bischler, by Niementowski, and by ourselves are identical in all respects with this compound of Weddige's, and the isomer represented by (1) is still unknown.

The conditions of our experiments resulting in the production of a quinazolon from anthranilic acid and nitriles were such that the first product of the reaction might be either a secondary amide, due to a condensation of the carboxyl and cyanogen groups or a transposition of groups might occur, giving anthranilic nitrile and acetic acid.<sup>1</sup> In the first case then, as our substance is identical with Weddige's, the reactions would be as follows :



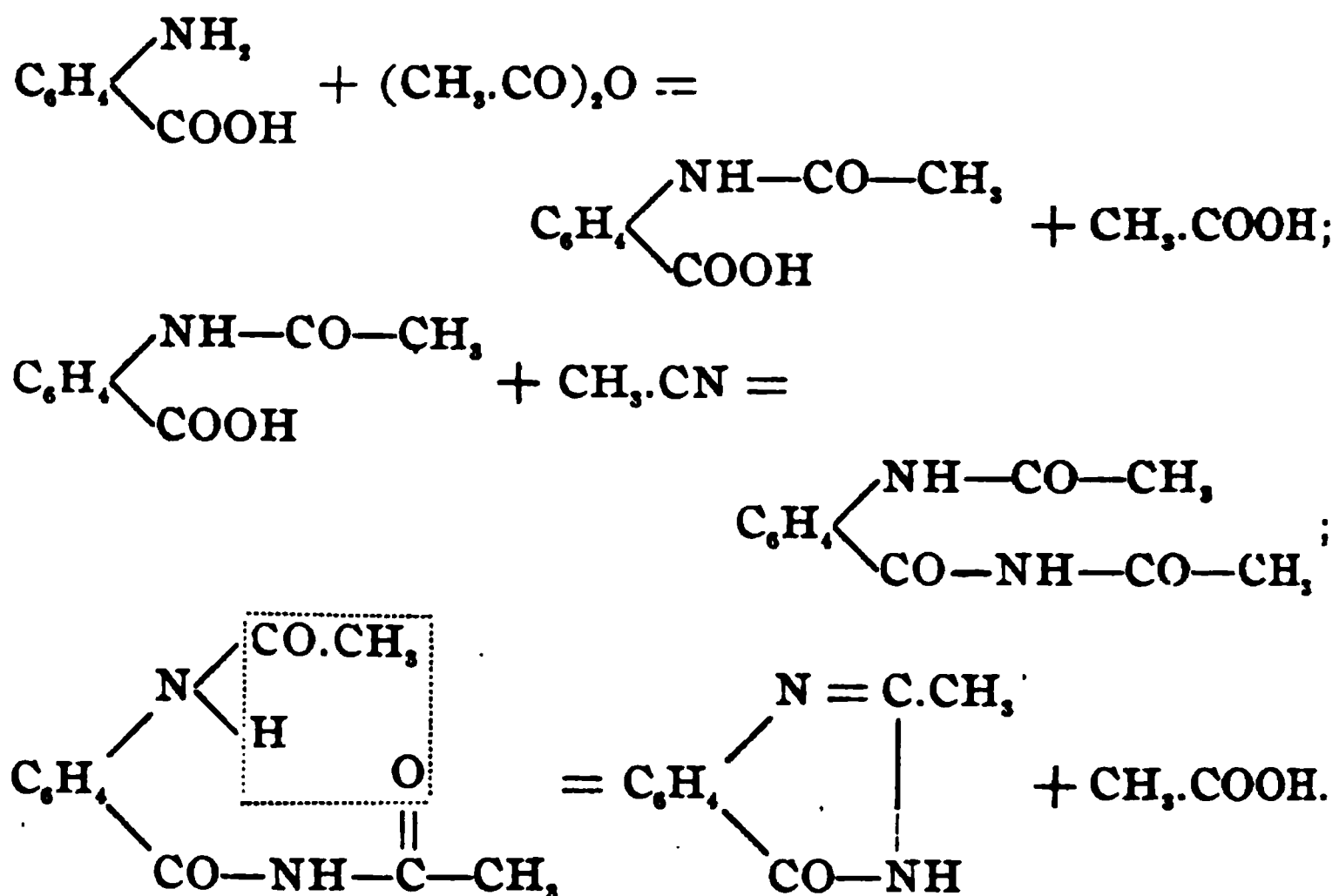
and not thus



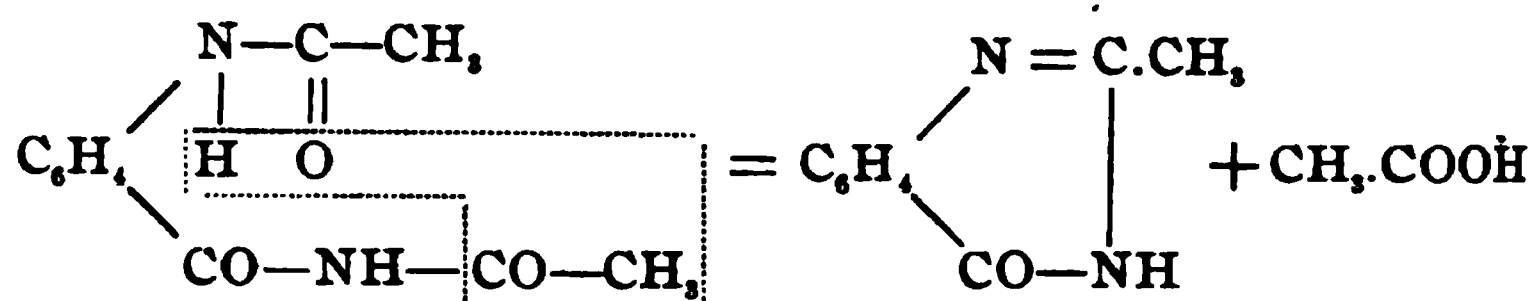
If this really represents the course of the reaction, it presents one or two interesting features. First, the elimination of water cannot here occur in the way described by Weddige, or an isomer would result with the double bond at (2) instead of at (1) as already mentioned. In regard to this point, however, it should be noted that this reaction is not exactly comparable with Weddige's, since in one case the condensation occurs with an aminic group, and in the other case with an amidic one. Another feature in which this synthesis differs from those already mentioned is in the position of the condensing acyl group, which here appears on the acid chain instead of in the amino group.

In later experiments, where acetic anhydride was present, the reactions would be similar :

<sup>1</sup> Compare Gautier: *Compt. rend.*, 67, 1255; and Colby and Dodge: *Am. Chem. J.*, 13, 1.

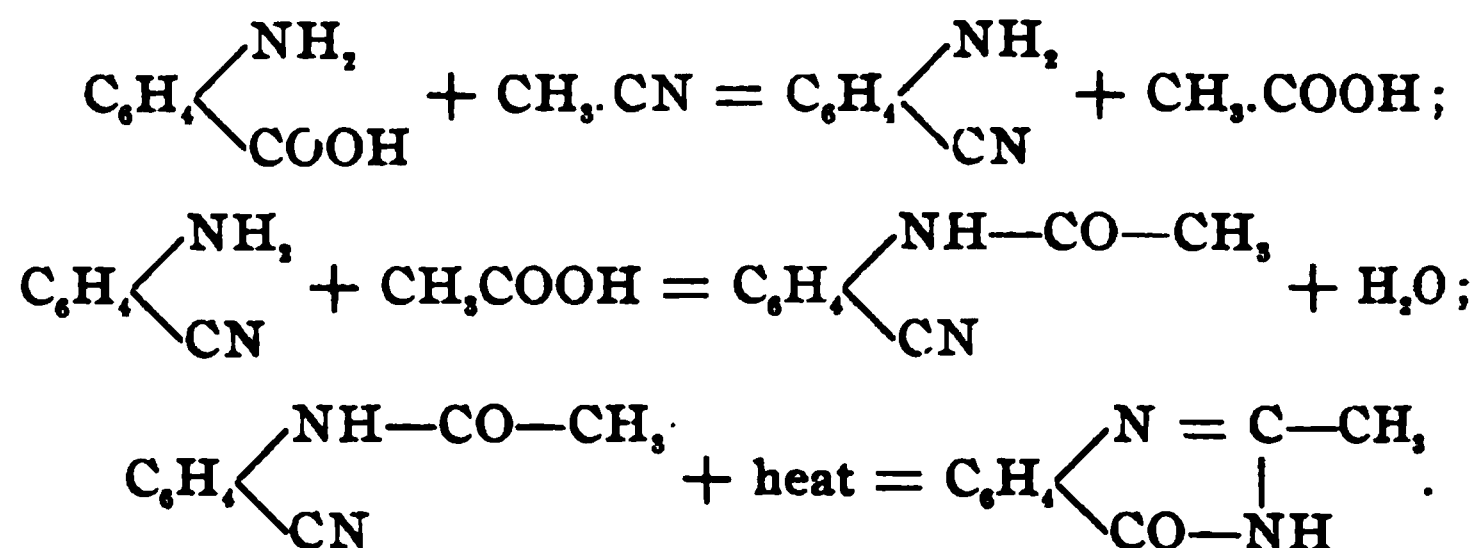


Although, in this case the possibility is not excluded of the reaction following the line indicated by Weddige :



In proof of the above reaction, acetylanthranilic acid was heated in a sealed tube with acetonitril, and the same quinazolon obtained.

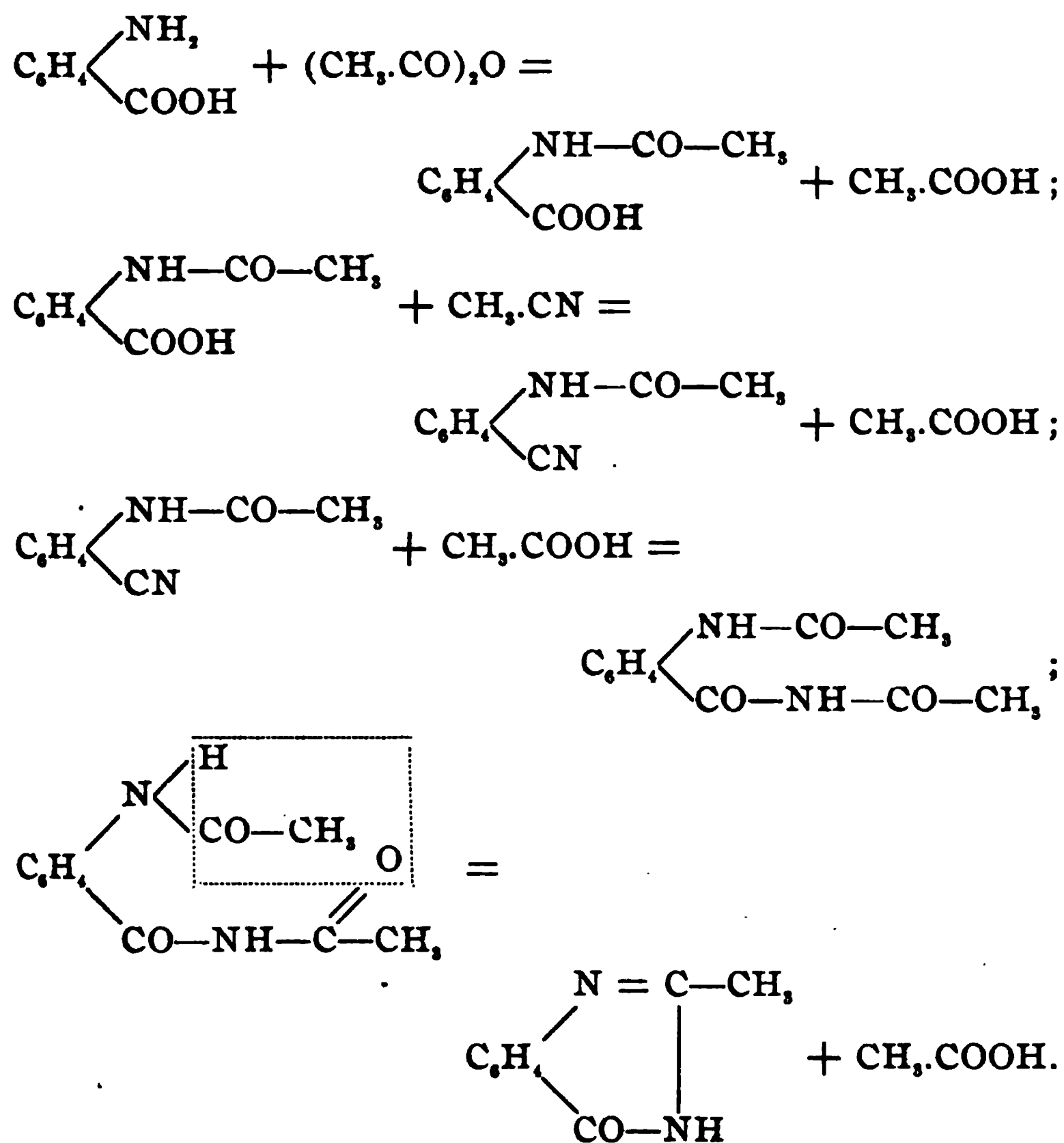
Another course which may be followed by the reaction is this:



The quinazolon being more stable at high temperatures than the anthranilic nitrile might cause such a rearrangement, but

Saemann,<sup>1</sup> who examined anthranilic nitrile, together with its acetyl and benzoyl derivatives, observed no such change. The production of anthranilic nitrile as the first phase of the reaction is more in accord with the results obtained by Colby and Dodge, but in some experiments carried out by us with the meta- and paraminobenzoic acids and acetonitrile we have been unable to isolate any aminobenzonitriles, although similar experiments with the three nitrobenzoic acids readily yielded the corresponding nitrobenzonitriles.

In our first experiments equal molecules of acid and nitrile were used, but in all of the later ones acetic anhydride was also added, and the reaction will then be slightly different :



<sup>1</sup> Ber. d. chem. Ges., 29, 631.

We, therefore, prepared some acetylanthranilic nitrile and heated it with acetic anhydride in a sealed tube, the result being the same quinazolon as before. Such a reaction is not likely to have taken place in the tubes where no acetic anhydride was used, for there would have been no excess of acetic acid to combine with the nitrile for the production of the secondary amid, the acetic acid reacting first, of course, with the amino group.

To sum up then, it seems most probable to us that the course of the reactions is as follows:

1. *In Absence of Acetic Anhydride*.—Condensation of the carboxyl and cyanogen groups to a secondary amide, which passes into the quinazolon by loss of water.

2. *In Presence of Acetic Anhydride*.—Production of acetylanthranilic acid, with subsequent combination of carboxyl and cyanogen groups, the resulting secondary amide yielding the quinazolon by loss of acetic acid.

#### EXPERIMENTAL PART.

Synthesis of 2-methyl-4-ketodihydroquinazolin from anthranilic acid and acetonitrile.

*Anthranilic Acid and Acetonitrile*.—One molecule of anthranilic acid and 2 or 3 molecules of acetonitrile were heated together in a sealed tube for six hours at 200°–210° C. The tube then contained a crystalline mass wet with a dark liquid, and when opened evolved carbon dioxide with considerable force. The mass was extracted with ether, and the ether solution filtered. On driving off the ether from the filtrate a brown oil remained together with a small amount of a crystalline substance. This oil was driven over with steam and found to be aniline, while the crystalline substance was identified as acetanilide. The carbon dioxide and aniline were the usual decomposition products of the anthranilic acid, the acetanilide being formed by a secondary reaction between aniline and acetic acid or aniline and acetamide.

The residue insoluble in ether consisted of needles which, recrystallized from water and bone-blackened, melted at 232°–233° C. (238°–239° C. corr.). These crystals were insoluble in cold water, soluble in hot, and partly soluble in hot chloroform. The

aqueous solution was acid to litmus, but did not decompose sodium carbonate solution, or dissolve freshly precipitated silver oxide when boiled with it. They readily dissolved in concentrated potassium hydroxide solution, but underwent no decomposition when the solution was boiled; but when this same alkaline solution was boiled with excess of concentrated hydrochloric acid and then cooled, long transparent needles of a hydrochloric acid salt were obtained, which sublimed before melting and gave the free base again (m. p.  $232^{\circ}$  C.) when treated with sodium carbonate solution. An aqueous solution of the free base gave the following reactions: with copper sulphate solution, a light blue precipitate; with silver nitrate solution, a white precipitate; with stannous chloride solution, a gelatinous precipitate, dissolving on heating and separating out in needles on cooling; with cobalt nitrate solution, a voluminous curdy precipitate, blue in presence of any excess of alkali; with mercuric chloride solution, a curdy white precipitate; with lead acetate solution, a curdy white precipitate. An aqueous solution of the hydrochloric acid salt gave a dark yellow precipitate with neutral potassium chromate, and an orange-red one with platinum chloride.

The free base crystallizes from water in transparent prisms or needles, carrying 1 molecule of water of crystallization which they readily lose at  $100^{\circ}$  C. An analysis of the crystals, dried at  $100^{\circ}$  C. gave the following results:

I. 0.1582 gram substance gave 0.3904 gram carbon dioxide, and 0.0711 gram water.

II. 0.1584 gram substance gave 0.3898 gram carbon dioxide, and 0.0722 gram water.

III. 0.1466 gram substance gave 0.3628 gram carbon dioxide, and 0.0666 gram water.

IV. 0.1613 gram substance gave 26 cc. nitrogen at  $24^{\circ}$  C. and 756 mm.

V. 0.1468 gram substance gave 23.8 cc. nitrogen at  $22.5^{\circ}$  C. and 750 mm.

	Calculated for $C_{12}H_8N_4O$	I.	II.	Found. III.	IV.	V.
Carbon.....	67.50	67.30	67.11	67.49	....	....
Hydrogen.....	5.00	4.99	5.06	5.04	....	....
Nitrogen.....	17.50	....	....	....	17.97	18.07
Oxygen.....	10.00	....	....	....	....	....
	<hr/> 100.00					

The molecular weight was also determined by the freezing-point method, using glacial acetic acid as the solvent :

Weight of substance taken.....	0.3184 gram.
"    " glacial acetic acid.....	23.7600 grams.
Freezing-point of acetic acid.....	4.05°
"    "    " mixture.....	3.71°
Lowering of freezing-point.....	0.34°
K.....	3880.0
Molecular weight .....	153.0
"    "    of $C_9H_8N_2O$ .....	160.0

The substance is hence identical with the 2-methyl-4-ketodihydroquinazolin of Weddige, Bischler, and Niementowski.

One of the first difficulties encountered in this synthesis is the tendency of the anthranilic acid to break up into carbon dioxide and aniline, and we have not been able as yet to overcome this entirely. Very gradual heating of the tube contents, even when long continued, did not appear to give any better yield than direct heating at 200°–210° C. for six or eight hours. The water split off in the reaction was also found to exert a most harmful influence upon the products, causing decomposition and the formation of much tar. The use of an excess of acetonitrile improved the yield somewhat, and the addition of acetic anhydride was found particularly beneficial in this respect. By using nearly enough anhydride to take up all the water split off, the yield was nearly doubled, being brought up to 45 per cent. of the theory, while the tube contents were invariably light colored and free from tar.

*Syntheses of Bischler and Burkart, and of Niementowski.*—For purposes of comparison some 2-methyl-4-ketodihydroquinazolin was prepared by the method of Bischler and Burkart, and of Niementowski.

*Bischler and Burkart's Synthesis.*—Acetylanthranilic acid was neutralized with ammonia, the solution evaporated to crystals, and the product recrystallized. Fusion of these crystals for twenty minutes gave a yield of the quinazolon amounting to about 25 per cent. of the weight of the acetylanthranilic acid used. Dehoff,<sup>1</sup> who was the first to suggest this method, abandoned it as unsatisfactory, but his difficulty seems to have been in getting a pure anthranilic acid to start with.

<sup>1</sup> *J. prakt. Chem.* [2], 42, 347.



*Niementowski's Synthesis.*—This investigator states that by fusing together acetamide and anthranilic acid for six to eight hours at  $135^{\circ}$ – $155^{\circ}$  C. a yield of quinazolon may be obtained equal to half the weight of the anthranilic acid used. Our experience indicated that twenty-four hours' heating at this temperature was necessary to remove all ammonia, and the yield of quinazolon was only about half that given by Niementowski. By treating the melt with ether the quinazolon remains insoluble and can thus be separated and recrystallized. In the ethereal washings we have isolated, in addition to acetanilide, a substance crystallizing from water in flat needles with jagged edges, and melting at  $190^{\circ}$ – $191^{\circ}$  C. ( $194^{\circ}$ – $195^{\circ}$  C. corr.). This melting-point could not be altered by repeated crystallizations, from water, and the substance cannot therefore be impure quinazolon. With metallic potassium or sodium the presence of nitrogen in this substance is easily demonstrated, but boiling with concentrated potassium hydroxide solution produces no ammonia, aniline, or other primary amine, for no isonitrile odor could be detected after the addition of chloroform, and it does not seem possible, therefore, that the compound can be amidic in character. That it probably represents an intermediate step in the reaction, however, is clearly shown by the fact that it can be converted to the quinazolon by boiling with concentrated hydrochloric acid or by sublimation. We are now endeavoring to prepare sufficient of this material to determine its structure, in the hope that it may throw considerable light upon the course of this interesting synthesis.

#### PREPARATION OF DERIVATIVES OF 2-METHYL-4-KETODIHYDRO-QUINAZOLIN.

Three sets of derivatives were prepared for purposes of comparison, one from quinazolon obtained by Bischler's synthesis, another from quinazolon obtained by Niementowski's synthesis, and a third set from our own product. An examination of similar derivatives in the three sets showed them in every case to be identical in all points irrespective of the source of the quinazolon.

*Hydrochloride.*—Prepared by boiling the free base, or its alkaline salts, with excess of concentrated hydrochloric acid. As the solution cools the hydrochloride crystallizes out in long trans-

parent needles, often of a decided yellowish cast and with a strong greenish fluorescence. These needles sublime without decomposition or dissociation, and do not break up at 336° C. as reported by Niementowski.<sup>1</sup>

*Chlorplatinate*.—By the addition of platinic chloride to a hot solution of the hydrochloride the chlorplatinate gradually separates on cooling in coarse red crystals, which can be recrystallized from water. Frequently unchanged hydrochloride will persistently separate with the chlorplatinate even after prolonged boiling with excess of platinum chloride.

	Calculated for (C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> O.HCl) <sub>2</sub> PtCl <sub>4</sub> .	Found.
	I.	II.
Pt .....	26.61	26.62 26.78

*Nitrate*.—When the free base is boiled with an excess of nitric acid (1 : 4), and the solution allowed to cool, the nitrate separates in white needles, which decompose at about 185° C. Niementowski found his product to decompose at 195° C.

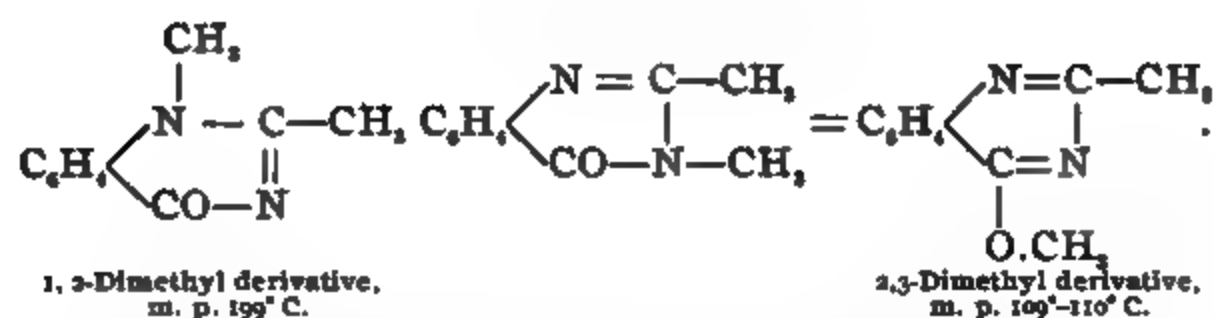
*Chromate*.—This salt was prepared both by the addition of potassium chromate to a solution of the hydrochloride, and also by heating the free base with chromic anhydride. It forms yellow crystals, beginning to blacken at 176° C. rather than at 182° C. as reported by Niementowski.

	Calculated for C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> O.CrO <sub>3</sub> .	Found.
Cr .....	20.00	19.41

*Methyl Ether*.—Equal molecules of 2-methyl-4-ketodihydroquinazolin, potassium hydroxide, and methyl iodide are dissolved in alcohol, and the mixture heated several hours on the water-bath with a return condenser. The alcohol is driven off, and the residue crystallized from water. It then forms white needles, melting at 71° C. (72° C. corr.) in the hydrated condition, and at 109°–110° C. (110°–111° C. corr.) when anhydrous, thus identifying it with the  $\beta,\gamma$ -dimethyl- $\Delta$ -pseudoxyquinazoline of Weddige,<sup>2</sup> and proving conclusively the structure of the original 2-methyl-4-ketodihydroquinazolin, for the isomeric pheno-2-methylhexadiazene(2)on(4) yields a dimethyl derivative melting at 199° C. The structure of these isomeric dimethyl derivatives is as follows:

<sup>1</sup> Ber. d. chem. Ges., 29, 1360.

<sup>2</sup> J. prakt. Chem. [2], 36, 151.



It seems most likely, in view of recent work upon similar compounds, that the 2-methyl-4-ketodihydroquinazolin reacts with alkalis in its pseudo or enolic form, and that the dimethyl derivative mentioned above contains the second methyl group attached to oxygen and not to nitrogen, thus giving an ether of a true methyl quinazolin. This would also explain why the 2,3-dimethyl derivative has a melting-point so much lower than its isomer, for in the 2-methyl-4-ketodihydroquinazolin compound with the double bond at (2) the carbonyl is para to the imido group, and it could not therefore so easily pass into a pseudo-enolic form.

#### SYNTHESIS OF 2-METHYL-4-KETODIHYDROQUINAZOLIN FROM ACETYLANTHRANILIC ACID.

*Acetylanthranilic Acid*.—This was prepared by the method of Jackson,<sup>1</sup> from anthranilic acid and acetic anhydride. Anthranilic acid was boiled for three hours with twice the theoretical amount of acetic anhydride. On cooling nothing separated, so the mixture was precipitated by pouring into water, the mass then warmed slightly to decompose any excess of anhydride, and the precipitate filtered out and washed. This precipitate was next dissolved in ammonia water, reprecipitated by hydrochloric acid, the precipitate filtered out and crystallized from water, when it formed plates melting at  $182^\circ\text{--}184^\circ \text{ C.}$  Occasionally it separated in a gelatinous mass on crystallization, showing a slightly lower melting-point ( $181^\circ\text{--}183^\circ \text{ C.}$ ), due possibly to difficulty in getting it perfectly dry.

In all cases, a small amount of the precipitate obtained by the addition of hydrochloric acid to the ammoniacal solution refused to dissolve in boiling water. This insoluble portion was separated and crystallized from glacial acetic acid, yielding fine white needles, melting at  $221^\circ\text{--}223^\circ \text{ C.}$  This is probably the diacetyl

<sup>1</sup> *Ber. d. chem. Ges.*, 14, 886.

derivative, but not enough was obtained for further investigation. Jackson,<sup>1</sup> reports similar results in his preparation of the acetylanthranilic acid.

*Diacetylanthranilic Acid.*—Bedson<sup>2</sup> states that when acetic anhydride and anthranilic acid are boiled together for some time under a return condenser the mixture solidifies on cooling to a crystalline mass of diacetylanthranilic acid. We have been unable to confirm this, as was the case apparently with Jackson also.

Anthranilic acid was boiled for several hours with acetic anhydride under a return condenser, but nothing separated on cooling. On addition of water a precipitate was obtained which, on recrystallization, proved to be impure monacetylanthranilic acid, melting at 175°–185° C. Another portion of anthranilic acid was heated with acetic anhydride until all excess of anhydride had been driven off. The residue was then dissolved in alcohol, the solution bone-blackened and evaporated, leaving a tarry mass from which hot benzene extracted a substance melting at 178°–182° C. on recrystallization, and which was evidently only impure monacetylanthranilic acid. Monacetylanthranilic acid was then boiled for ten hours with acetic anhydride, decomposition apparently setting in at this point, for when the mass was poured into water it produced a yellow milky solution with much tar.

The effect of pressure was next tried. Five grams of anthranilic acid, 9 cc. of acetic anhydride, and 10 cc. glacial acetic acid, were heated together in a sealed tube for five hours at 160°–170° C. The contents of the tube then appeared liquid, and no pressure was detected on opening the tube. The excess of acetic acid and anhydride was removed by distillation, and the residue left in a desiccator over potassium hydroxide, where it gradually solidified to a crystalline mass, some of which recrystallized from benzene melted at 180°–182° C. and proved to be the monacetyl derivative again. We have, therefore, failed to get any appreciable amount of diacetylanthranilic acid by the methods employed.

*Acetylanthranilic Acid and Acetonitrile.*—Five grams of acetylanthranilic acid and 7 cc. acetonitrile were heated together in a sealed tube for four and a half hours at 220°–210° C. The tube

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *J. Chem. Soc.*, 37, 756.

was then filled with needle crystals and a dark brown liquid. No pressure was evident upon opening the tube. The liquid was decanted carefully from the crystals and the latter washed with dilute sodium carbonate solution, to remove unchanged acid, etc. The residual crystals dissolved in alcohol, bone-blackened, and the solution evaporated, yielded coarse needles melting at  $232^{\circ}$ – $236^{\circ}$  C. and readily identified with the 2-methyl-4-ketodihydroquinazolin prepared by the methods already mentioned.

To prove that no acetyl derivative of the quinazolon was produced in this reaction, 0.5 gram of the quinazolon was boiled for one hour with 5 cc. acetic anhydride, and on cooling long needles separated exactly similar to those obtained from the above reaction. That these were really only the original quinazolon was shown by the molecular weight determination, by the freezing-point method, with glacial acid as the solvent:

Weight of substance .....	0.4637 gram.
" " acetic acid .....	23.3805 grams.
Freezing-point of acetic acid .....	$4.04^{\circ}$
" " " mixture .....	$3.57^{\circ}$
Lowering of freezing-point .....	$0.47^{\circ}$
K .....	3880.0
Molecular weight .....	163.7
" " of $C_9H_8N_2O$ .....	160.0
" " " $C_9H_7N_2O(CO.CH_3)$ .....	202.0

Acetyl chloride was found to have no action upon the quinazolon under ordinary conditions.

The experiments with anthranilic nitrile, acetylanthranilic nitrile, and similar orthoaminonitriles, form the subject of another paper.

In conclusion, then, the following new syntheses of 2-methyl-4-ketodihydroquinazolin have been discovered:

1. By heating orthoamino acids, or their acyl derivatives, with nitriles.
2. By heating orthoaminonitriles, or their acyl derivatives, with acids.

The extension of these syntheses to other acids and nitriles is now under way. We are also studying the action of nitriles upon  $\alpha$ - and  $\beta$ -amino acids and their nitriles both aliphatic and aromatic, as well as the action of nitriles upon other classes of orthosubstituted acids.

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## THE JOURNAL

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CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA  
UNIVERSITY, No. 27.]

## NOTES ON LEAD AND CADMIUM FERROCYANIDES.

BY EDMUND H. MILLER AND HENRY FISHER.

Received June 29, 1900.

## LEAD FERROCYANIDE.

THE following series of experiments were made in order to ascertain whether the composition of lead ferrocyanide is variably  $\text{Pb}_2\text{Fe}(\text{CN})_6$ , or whether, like the ferrocyanides of manganese and zinc, it is affected by the conditions of precipitation.

The precipitates were made as follows: Lead acetate was dissolved in water and heated to boiling, to this a hot aqueous solution of potassium ferrocyanide was added, and acid in some cases is noted later. The precipitates were allowed to settle and were washed by decantation until free from lead or ferrocyanide as indicated by hydrogen sulphide, or by ferric chloride. They were then dried at  $105^\circ \text{C}$ . to constant weight. The method of analysis was in all cases as follows: About one gram was dissolved in dilute nitric acid in a casserole, and after the addition of sulphuric acid, evaporated to fumes. One evaporation was found to effect complete decomposition. The residue was taken

up with 1 per cent. sulphuric acid to which half its volume of alcohol was added. The lead sulphate was washed with 1 per cent. sulphuric acid containing alcohol, filtered and weighed in a Gooch crucible. The iron was precipitated in the filtrate by ammonia, after boiling out the alcohol and adding ammonium chloride, filtered, washed, and weighed as  $\text{Fe}_2\text{O}_3$ . The filtrate from the iron was evaporated to dryness in platinum, the ammonia salts volatilized and the potassium sulphate weighed.

A. Precipitate formed in a neutral solution with lead in excess, settles rapidly. The analytical results are :

	I.	II.	III.	Average.
Lead .....	66.03	66.15	66.09	66.09
$\text{Fe}(\text{CN})_6$ .....	34.07	33.98	33.85	33.97
Potassium.....	0.50	0.48	0.45	0.47
				<hr/> 100.53

B. Solution neutral, ferrocyanide in excess, the precipitate settles slowly. It gave on analysis :

	I.	II.	III.	Average.
Lead .....	66.26	66.06	65.98	66.10
$\text{Fe}(\text{CN})_6$ .....	33.54	33.77	33.90	33.70
Potassium.....	0.62	0.55	0.58	0.58
				<hr/> 100.38

C. Solution slightly acid with acetic acid, lead in excess. The precipitate settles rapidly. On analysis the following results were obtained :

	I.	II.	III.	Average.
Lead .....	64.42	64.55	64.62	64.53
$\text{Fe}(\text{CN})_6$ .....	35.48	35.33	35.37	35.39
Potassium.....	0.84	0.81	0.80	0.82
				<hr/> 100.74

D. Solution slightly acid with acetic acid, ferrocyanide in excess. Precipitate settles rapidly. The results on analysis were almost identical with those obtained from the preceding precipitate.

	I.	II.	III.	IV.	Average.
Lead .....	64.43	64.28	64.38	64.58	64.42
$\text{Fe}(\text{CN})_6$ .....	35.47	35.62	35.69	35.60	35.59
Potassium .....	0.82	0.76	0.86	0.79	0.81
					<hr/> 100.82



E. Solution strongly acid with acetic acid, ferrocyanide in excess. Precipitate settles badly. The results are :

	I.	II.	Average.
Lead.....	63.73	64.02	63.87
Fe(CN) <sub>6</sub> .....	35.51	35.02	35.26
Potassium .....	0.76	0.96	0.86

These and the following are results calculated from the determination of potassium, lead, and iron in undried portions and consequently, when calculated from the ratio of Fe : K : Pb, add up to 100 per cent.

F. Solution strongly acid with hydrochloric acid, ferrocyanide in excess, precipitated hot as usual.

	I.	II.	Average.
Lead.....	63.02	63.39	63.21
Fe(CN) <sub>6</sub> .....	34.74	34.48	34.61
Potassium .....	2.24	2.12	2.18

When the analysis is made on a sample dried to constant weight, it invariably adds up to a little over 100 per cent. This is probably caused by the fact that on drying, the precipitates become either bluish or greenish in color due to a slight decomposition so that the percentages of Fe(CN)<sub>6</sub>, which are calculated from the iron are high.<sup>1</sup>

It is evident from these results that the precipitate varies in composition under different conditions of precipitation, and as the acidity increases the percentage of potassium increases and that of lead diminishes.

Also, that when the acidity is the same the composition is the same whether ferrocyanide or lead is in excess.

Berzelius<sup>2</sup> states that when formed in a neutral solution with potassium ferrocyanide in excess, the composition of the precipitate is Pb<sub>2</sub>Fe(CN)<sub>6</sub>. Using the most recent atomic weights this corresponds to a percentage composition of:

Lead .....	66.10
Fe(CN) <sub>6</sub> .....	33.90

Our results are, with lead in excess :

Lead .....	66.09
Fe(CN) <sub>6</sub> .....	33.97

<sup>1</sup> For the CN : Fe ratio is higher in Fe(CN)<sub>6</sub> than in Fe<sub>7</sub>(CN)<sub>12</sub> or Fe<sub>8</sub>(CN)<sub>12</sub>.

<sup>2</sup> *Ann. Chem. Phys.*, 15, 157 (1820).

With ferrocyanide in excess :

Lead .....	66.10
Fe(CN) <sub>6</sub> .....	33.70

The only statement we have found suggesting any variation in the composition of this ferrocyanide is by Gay-Lussac<sup>1</sup> that "the precipitate for however long a time it may have been washed, retains from 6-9 per cent. of ferrocyanide of potassium; of which it continues to give up a certain quantity to fresh portions of water." The conditions of this precipitation are not stated.

In order to compare these results with those obtained by titration, the following experiments were made. A solution of potassium ferrocyanide was very carefully standardized against metallic zinc and freshly ignited zinc oxide. The conditions being; bulk 200 cc., acidity 2 cc. concentrated hydrochloric acid, temperature about 80° C. Uranium acetate was used as an indicator on porcelain. An allowance of 0.3 cc. was made in each case for the excess necessary to affect the indicator. The results of six concordant determinations gave as the strength of this solution, 1 cc. = 0.005857 gram of zinc.

This solution was then used to titrate solutions containing known weights of lead as follows :

*Neutral Solution.*—Separate portions of metallic lead, of about 1 gram each, were dissolved in nitric acid, hydrochloric acid added and evaporated to complete dryness; the lead chloride was then dissolved in hot water diluted to 200 cc. and titrated. The titration in a neutral solution is not altogether satisfactory. Five determinations gave results varying from 0.02454 to 0.02461. Average, 0.02458.

*Acetic Acid Solution.*—Six determinations gave from 0.02450 to 0.02458; the average coinciding with the two most satisfactory titrations is 0.02454 gram.

*Hydrochloric Acid Solution.*—In a solution containing one drop of concentrated hydrochloric acid the results were from 0.02441 to 0.02446; average, 0.02444 gram. With 1 cc. of hydrochloric acid the results were unreliable on account of the solubility of the precipitate.

<sup>1</sup> Gmelin's "Handbook of Chemistry" (London, 1852), Vol. VII, p. 490.

Assuming that the precipitates formed are in one case  $\text{Zn}_3\text{K}_4(\text{Fe}(\text{CN})_6)_2$ , and in the other  $\text{Pb}_3\text{Fe}(\text{CN})_6$ , or that amount of ferrocyanide which precipitates three atoms of zinc precipitates four of lead, the factor by which the zinc standard must be multiplied to give the lead standard is 4.218. This gives by calculation from the zinc standard, 0.0247 as the lead standard of the solution.

The amounts of lead precipitated per cubic centimeter in all cases reach this value and although the variations are not so great as is shown from the analyses of the precipitates, they are exactly the same order, and so confirm the statement that the increase of acidity tends to diminish the percentage of lead in the precipitate.

Our results agree closely with Low's<sup>1</sup> statement: that a solution containing 10 grams per liter of crystallized potassium ferrocyanide will equal 10 milligrams of lead per cubic centimeter and are at complete variance with a statement by Furman<sup>2</sup> that it requires 16 grams per liter for such a solution. Furman's figure is evidently based on the assumption that this value can be determined by a direct ratio between lead and zinc.

#### CADMIUM FERROCYANIDE.

The potassium ferrocyanide solution, already described, was used to titrate a number of solutions containing cadmium under different conditions. Portions of cadmium oxide of 0.3 to 0.6 gram each were dissolved in hydrochloric acid, and evaporated to complete dryness, then dissolved in 200 cc. of hot water and titrated. It was found that uranium acetate on porcelain was very unsatisfactory as the precipitate reacts with the indicator as is the case with manganese, so that the end tests in these titrations were made on filter-paper placing the drops so that the precipitate of cadmium ferrocyanide did not come in contact with the uranium acetate.

The results in a neutral solution were not concordant, varying between 0.0071 and 0.00727 gram of cadmium per cubic centimeter.

In a solution containing 1 cc. of 50 per cent. acetic acid the

<sup>1</sup> This Journal, 15, 550 (1893).

<sup>2</sup> "Manual of Practical Assaying," p. 139.

results ran from 0.00699 to 0.00702 gram of cadmium; average, 0.0070 gram.

In a solution containing 1 to 2 cc. of concentrated hydrochloric acid the average of six determinations on cadmium oxide gave 1 cc. = 0.007177 gram of cadmium; this was checked by four tests with metallic cadmium which gave 0.007165 gram, or a general average of 0.00717 gram. Another set was made with only a few drops of hydrochloric acid present; these gave almost the same results. With this solution it was found possible to use uranium acetate on porcelain but drops on filter-paper are a safer end-point for cadmium titrations.

As cadmium hydroxide is soluble in ammonia it was possible to extend the titration to an ammoniacal solution by using as an indicator a 4 per cent. solution of copper sulphate, as recommended by Moldenhauer<sup>1</sup> for zinc. The spots are made on filter-paper, as already described; the end-point, a red line, is distinct but not as delicate as with uranium acetate. An allowance of 0.9 cc. was made for the excess necessary to affect the indicator. Four tests gave the following values for 1 cc.: 0.00669, 0.00678, 0.00674, 0.00674; average, 0.00674 gram of cadmium per cubic centimeter.

The formula usually assigned to cadmium ferrocyanide is that given by Hermann:<sup>2</sup>  $\text{CdK}_2\text{Fe}(\text{CN})_6$ ; assuming that this is the composition of the precipitate, the ratio as regards ferrocyanide is  $3\text{Zn} = 2\text{Cd}$ , and the strength of the ferrocyanide solution used would be 1 cc. = 0.00671 gram cadmium. The results of the titrations do not agree with this value except those obtained in an ammoniacal solution.

Other formulas have been given for cadmium ferrocyanide. Dammer gives it the normal composition  $\text{Cd}_2\text{Fe}(\text{CN})_6$  and cites Wittstein<sup>3</sup> as his authority, but the original article gives neither formula nor analysis.

Wyrouboff<sup>4</sup> gives the composition under all conditions as  $\text{K}_5\text{Cd}_5(\text{Fe}(\text{CN})_6)_4$ , which has been altered in Comey's "Dictionary," so as to satisfy the valence of the  $\text{Fe}(\text{CN})_6$  radical to  $\text{K}_6\text{Cd}_5(\text{Fe}(\text{CN})_6)_4$ . Assuming that this is the precipitate formed, the

<sup>1</sup> *Chem. Ztg.*, 13, 1220 (1889), and 15, 223 (1891).

<sup>2</sup> *Ann. Chem. u. Pharm.*, 145, 235 (1868).

<sup>3</sup> *Büchner's Repertorium der Pharm.*, 63, 316-317.

<sup>4</sup> *Ann. chim. phys.* [5], 8, 449 (1878).

ratio as regards ferrocyanide becomes  $6\text{Zn} = 5\text{Cd}$ , and the strength of the solution used would be 1 cc. = 0.00838 gram cadmium.

Our results in acid solutions are intermediate between these values and indicate a variation in the composition of the precipitate between the formulas of Hermann and of Wyruboff. They are confirmed by a statement by Mackay<sup>1</sup> that it requires about  $\frac{1}{4}$  per cent. less potassium ferrocyanide to precipitate cadmium than is required by the formula  $\text{CdK}_4\text{Fe}(\text{CN})_6$ , or in other words the cadmium standard is higher than would be obtained by calculation. They are again in direct contradiction to the statement by Furman that the cadmium standard can be obtained from the zinc standard by direct proportion assuming that  $2\text{Zn} = 2\text{Cd}$ .

In order to ascertain the composition of cadmium ferrocyanide under different conditions analyses of the precipitates must, of course, be made. This work has already been started and while no results have yet been obtained the marked difference in the physical properties of the precipitates seems to confirm the variation in composition.

COLUMBIA UNIVERSITY,  
JUNE 27, 1900.

[CONTRIBUTION FROM THE LABORATORY OF THE NORTH CAROLINA  
AGRICULTURAL EXPERIMENT STATION.]

## THE DIGESTIBILITY OF SOME NON-NITROGENOUS CON- STITUENTS OF CERTAIN FEEDING-STUFFS.<sup>2</sup>

BY G. S. FRAPS.

Received June 16, 1900.

THE ether extract, protein, nitrogen-free extract, and crude fiber, which are determined in ordinary feeding-stuff analyses, are groups of compounds, and are composed of various substances with different properties and different coefficients of digestibility. The ether extract may contain (besides the true fats) waxes, cholesterin, phytosterin, lecithin, hydrocarbons, coloring-matters, etc. "Protein" includes amido compounds, acid amides, organic bases, ammonia, and nitrates, besides proteids of varied nature, one of which, nuclein, is entirely indiges-

<sup>1</sup> This Journal, 21, 940 (1899).

<sup>2</sup> This work was suggested to the author by Prof. W. A. Withers, Chemist of the Station. See Bulletin 172.

tible. The nitrogen-free extract may contain sugars, dextrin, gums, starches, pentosans, coloring-matters, organic acids, lignocellulose and cellulose, the two latter remaining in part in the crude fiber. The crude fiber contains cellulose, lignocellulose, etc. Considering the number of substances which may enter into the composition of the fodder-groups, and the variations which take place in the quantity present, it is not surprising that the digestibility of these groups differs greatly with different feeding-stuffs.

The digestibility of some of the proximate constituents of feeding-stuffs has been determined, or, more correctly, groups of proximate constituents, namely, the sugar group, the starch group, and the pentosan group. All three of these groups have not been determined on the same material. The work about to be described in this paper has given a basis for calculating the digestibility of certain proximate groups, which can be arranged in the following tentative order, according to their digestibility: Sugars, starches, pentosans, crude fiber, residual nitrogen-free extract, and pentosans in the crude fiber. The number of digestion experiments made is not large, but it is not believed that future experiments will materially modify the order above given. This Station expects to continue the work along this line.

The materials used in this work are from digestion experiments on sheep, one described in Bulletin 148 of this Station, six described in Bulletin 160, one not yet published. Excepting timothy hay No. 1, all figures are means of experiments with two sheep.

#### DIGESTIBILITY OF SUGARS.

W. H. Jordan, J. M. Bartlett, and L. H. Merrill, at the Maine Experiment Station,<sup>1</sup> found that the sucrose and reducing sugars in alsike clover, white clover, blue joint, orchard grass, red top, timothy, wild oat grass, witch grass, buttercup, and white weed were completely digested. E. F. Ladd, at the New York (Geneva) Experiment Station,<sup>2</sup> found the sucrose and reducing sugars to be completely digested in alfalfa hay, mixed hay, wheat bran, corn-meal, cottonseed-meal, linseed-meal, and oats; the

<sup>1</sup> Report 1888, 98.

<sup>2</sup> Report 1889, 149.

sucrose in turnips fed with mixed hay was digested only 78.7 per cent., the reducing sugars being completely digested. B. W. Kilgore and F. E. Emery, at the North Carolina Station,<sup>1</sup> found the reducing sugars completely digested in corn-fodder, crimson clover hay, cowpea vine hay, soja-bean silage, cottonseed, and cottonseed hulls. H. C. Sherman<sup>2</sup> found the glucose and sucrose (soluble carbohydrates) of wheat bran digested 96.7 per cent., the feces containing 0.7 per cent.

Twenty-three excrements from a number of digestion experiments made at this Station were tested for sugars in the usual way, after treating the solution with lead acetate. In twelve of them, traces of copper were reduced, corresponding to from 0.05 to 0.20 per cent. of sugars, with a mean of 0.09 per cent. This reduction is not believed to be caused by sugars, but by other reducing matters, as is plain from the following experiment. Excrement 1376, from corn silage, giving 0.15 per cent. apparent sugars; excrement 1377, from corn silage, 0.05 per cent. sugars; excrement 1411, from timothy hay, 0.20 per cent. sugars; and excrement 1437, from sorghum fodder, 0.14 per cent. sugars were taken. Fifty grams of each were digested with 500 cc. cold water, filtered, and washed with about 1000 cc. water. Basic lead acetate was added in excess, filtered, and the filtrate evaporated to about 25 cc. on a water-bath, organic matter separating. The lead was removed with sodium carbonate, filtered off, and the filtrate made up to 100 cc. Twenty-five cc. corresponding to 12.5 grams excrement, and about seventeen times as much as was used in the preliminary test, gave no trace of either sucrose or dextrose in any of the four excrements. The reducing substances probably separated during the evaporation. The traces of copper oxide were probably not due to reduction by sugars.

The twenty-three excrements were as follows: From crabgrass hay, crabgrass hay and pea-meal (2), crabgrass hay and corn bran (2), green rape (3), crabgrass hay and rice bran (2), cat tail millet (2), sorghum fodder (2), crimson-clover hay, soja-bean silage, corn silage (4), timothy hay (2), corn fodder. 1

<sup>1</sup> Technical Bulletin No. 4.

<sup>2</sup> This Journal, 19, 291.

the twelve materials and twenty-three experiments, sucrose and reducing sugars were completely digested.

Taking all the experiments into consideration, it is found that in thirty materials and forty-one experiments, reducing sugars are invariably digested completely, and in twenty-eight of the thirty materials, and thirty-nine of the forty-one experiments, sucrose is completely digested. The assertion that sugars are, as a rule, completely digested may be taken as established.

The determination of sugars is important with hays, and cottonseed-meal; less so in the case of the starchy foods. Hays contain a moderate amount of sugars; for example,<sup>1</sup> red clover (average of 21) contains 6.36 per cent., timothy hay (average of 21) 8.44 per cent., sorghum 21 per cent., corn fodder 3.9 per cent.; cottonseed-meal contains 9.22 and 7.94 per cent. raffinose, being 33.5 and 32.9 per cent. of the nitrogen-free extract, respectively. If the sugar in the hays is subtracted from the nitrogen-free extract, and then the digestibility of the latter is calculated, a considerable decrease is often found. The digestibility of nitrogen-free extract, containing sugars, is 71.8 in alfalfa hay; if sugar is subtracted, it is 68.5, a decrease of 4.6 per cent. With mixed hay, the decrease is from 55.5 to 40.4, a decrease of 27 per cent.; with timothy hay, from 60.3 to 53.5, or 11 per cent., and 56.2 to 51.1, or 9.1 per cent.; with green rape, from 93.8 to 92.5, or 1.4 per cent.; and with cottonseed-meal, from 61.5 to 42.5, the enormous decrease of 31 per cent. These figures may serve to emphasize the importance of determining sugars. The calculations and details of all these experiments are published in Bulletin No. 172 of this Station.

#### DIGESTIBILITY OF PENTOSANS.

The furfural produced by distillation of feeding-stuffs with hydrochloric acid comes, for the most part, from pentosans; *i. e.*, bodies which yield pentose sugars on hydrolysis. Other bodies than true pentosans are found in plants, which are decomposed with formation of furfural, such as the oxycelluloses and lignocelluloses. The latter are usually described as mixtures of cellulose and incrusting substance, or lignin.

The true pentosans are, presumably, dissolved by dilute acids

<sup>1</sup> E. F. Ladd: *Am. Chem. J.*, 10, 49.



d alkalies, and hence are contained in the nitrogen-free extract, but the oxycelluloses and lignocelluloses are partly attacked by these reagents also. The furfural from the crude extract may be considered as originating from the latter bodies, to which the name pseudopentosans may be given.

W. E. Stone<sup>1</sup> determined the digestibility of total pentosans in a number of feeding-stuffs, titrating the furfural distillate with phenylhydrazine, and using Fehling's solution as an indicator. The per cent. of pentosans digested was found to be: in timothy hay, 48.0 and 49.5 per cent.; ditto early bloom, 60.4 and 54.6 per cent.; ditto late cut, 62.8 and 48.2 per cent.; *Anthoxanthus spicata*, 68.6 per cent.; *Agrostis vulgaris*, 70 per cent.; *Calamagrostis canadensis* 90.4 per cent.; *Triticum repens*, 59.9 per cent.; Hungarian grass, 68.2 per cent.; *Trifolium hybridum*, 56.8 per cent.; corn fodder, northern, 76.6 per cent.; ditto southern corn, 69.6 per cent.; timothy hay and sugar-beets, 71.3 per cent.; timothy hay and rutabagas, 57.1 per cent.; timothy hay and wheat bran, 45.6 per cent.; timothy hay and gluten meal, 59.1 per cent.; *Agrostis vulgaris* and wheat bran, 54.1 per cent.; ditto and wheat middlings, 64.9 per cent. Excluding *Calamagrostis canadensis*, the average digestibility of the pentosans in the nineteen substances is 60.3 per cent., with a minimum of 45.6 and a maximum of 71.3 per cent.

J. B. Lindsay and E. B. Holland<sup>2</sup> have determined the digestibility of pentosans in the following materials: Hay of mixed grasses, (a) 63 per cent., (b) 62 per cent.; Buffalo gluten feed, 88 per cent.; new process linseed-meal, 89 per cent.; old process linseed-meal, 84 per cent.; corn cobs, 62 per cent.; dried brewer's grains, 55 per cent.; spring-wheat bran, 62 per cent.; winter-wheat bran, 64 per cent. The mean is 68.8 per cent.

H. C. Sherman<sup>3</sup> found the digestibility of pentosans in wheat bran to be 66.2 per cent.

Determination of the total pentosans and pentosans in the crude fiber (pseudopentosans) have been made in feeding-stuffs, wastes, and excrements from digestion experiments made at this Station. The method of determining pentosans used is, in

<sup>1</sup> *Agr. Science*, 7, 6.

<sup>2</sup> *Ibid.*, 8, 172.

<sup>3</sup> *This Journal*, 19, 308.

brief, as follows: Three grams of substance in a side-necked flask on a wire gauze are distilled with 100 cc. of hydrochloric acid of 1.06 specific gravity. When 30 cc. have distilled over, 30 cc. of the acid are run into the flask through a separatory funnel in such a manner as to wash down the particles on its sides. The distillation is continued in this manner until the volume of the distillate is 360 cc. A sufficient quantity of phloroglucinol to precipitate all the furfural, is added, the volume made up to 500 cc., the precipitate collected on a Gooch filter, washed with 100 cc. water, dried to constant weight at 100°, and weighed. The time required to dry the precipitate is from seven to nine hours. Commercial phloroglucinol is used, and is purified by dissolving it in hydrochloric acid of 1.06 specific gravity and allowing the diresorcinol to crystallize out.

In the case of crude fiber, three grams of material were treated, in the usual way for the determination of crude fiber using, however, 300 cc. of the acid and 300 cc. of the alkali. The fiber was then distilled with acid, as described above.

The composition of the feeding-stuffs is given in the table.

#### COMPOSITION OF FEEDING-STUFFS.

(Dry Matter.)

	Sugars.	Total pentosans.	Pentosans.	Pseudo- pentosans.	Residual N-free extract.
Timothy hay No. 1.....	8.33	24.86	19.71	5.15	16.88
Crabgrass hay No. 1.....	1.89	26.25	21.90	4.35	21.40
Crabgrass hay No. 2.....	2.20	24.71	19.85	4.85	24.09
Cowpea-meal.....	5.66	6.83	6.83	0	52.20
Corn bran.....	2.93	25.15	25.15	0	41.36
Green rape No. 1.....	8.41	10.57	9.57	1.00	29.81
Green rape No. 2.....	7.03	8.71	8.04	0.67	26.04
Rice bran.....	1.56	10.88	9.88	1.00	40.31
Cottonseed-meal.....	7.94	7.83	....	....	....

The pentosans in the crude fiber is, in timothy hay No. 1, 20.7 per cent. of the total pentosans; in timothy hay No. 2, 20.5 per cent.; in crabgrass hay No. 1, 18.4 per cent.; in crabgrass hay No. 2, 19.6 per cent.; in cowpea-meal and corn bran, none; in green rape No. 1, 9.5 per cent.; in green rape No. 2, 7.7 per cent., and in rice bran, 9.2 per cent. It is apparent that the crude fiber of hays contains a large percentage of the pentosans. The pentosans are distributed between the crude fiber and the nitrogen-free extract. The pentosans in the crude fiber

not here regarded as true pentosans, but are called pseudopentosans; they are different from the pentosans in the nitrogen-free extract, although the line of separation between the two is arbitrary one. The distribution and digestibility of the pentosans are given in the table. It is seen that from 0 to 21 per cent. of the pentosans are pseudopentosans, and that in four of five cases the pseudopentosans are less digestible than the pentosans in the nitrogen-free extract. The digestibility of the total pentosans varies from 53 to 95 per cent.

## DISTRIBUTION AND DIGESTIBILITY OF PENTOSANS.

	Of 100 parts pentosans		Digestibility of pentosans.		
	True	Pseudo-	Total	True	Pseudo-
Timothy hay No. 1.....	79.3	20.7	55.8	58.1	46.9
Timothy hay No. 2.....	79.5	20.5	55.9	57.0	52.0
Crabgrass hay No. 1.....	81.6	18.4	63.1	61.0	69.9
Crabgrass hay No. 2.....	80.4	19.6	....	....	....
Sowpea-meal <sup>1</sup> .....	100.0	0	76.1	76.1	....
Corn bran <sup>1</sup> .....	100.0	0	71.6	71.6	....
Green rape No. 1.....	90.5	9.5	94.6	95.7	84.6
Green rape No. 2.....	92.3	7.7	91.9	93.2	75.9
Rice bran <sup>1</sup> .....	90.8	9.2	53.5	57.3	....

## DIGESTIBILITY OF NITROGEN-FREE EXTRACT.

The composition and digestibility of the nitrogen-free extract is given in the table below. The residual nitrogen-free extract is the total nitrogen-free extract less sugars and pentosans. It varies in quantity from 47 to 85 per cent. of the nitrogen-free extract.

## COMPOSITION AND DIGESTIBILITY OF NITROGEN-FREE EXTRACT.

	In 100 parts			Digestibility.	
	Sugars.	Pentosans.	Residue.	Pent- osans.	Resi- due.
Timothy hay No. 1.....	14.9	35.2	49.9	58.1	50.1
Timothy hay No. 2.....	10.5	41.6	47.9	57.0	46.0
Crabgrass hay No. 1.....	4.2	48.4	47.4	61.0	32.7
Crabgrass Hay No. 2.....	4.8	43.0	52.2	....	....
Sowpea-meal <sup>2</sup> .....	4.8	10.6	84.6	76.1	97.4
Corn bran <sup>2</sup> .....	4.2	36.2	59.6	71.6	86.1
Green rape No. 1.....	15.2	20.6	64.2	95.7	91.4
Green rape No. 2.....	19.8	18.9	61.3	93.2	86.5
Rice bran <sup>2</sup> .....	3.0	19.1	77.9	57.3	85.0

<sup>1</sup> Calculated from ration with crabgrass hay.

<sup>2</sup> Digestibility calculated from ration with crabgrass hay.

In the timothy hays, the crabgrass hay, and the green rape, the order of digestibility is: sugars, pentosans, residue. In the cowpea-meal, the corn bran, and the rice bran, the order is: sugars, residue, pentosans, but this residue consists most largely, if not entirely of starch, so that we may say that starch is more digestible than pentosans. The order of digestibility of the components of the nitrogen-free extract is, then,—sugars, starch, pentosans, and residue.

#### DIGESTIBILITY OF CRUDE FIBER.

Crude fiber contains from 0 to 21 per cent. of the total pentosans, sometimes as much as 42 per cent.<sup>1</sup> The table below exhibits the composition and digestibility of the crude fiber. In four of the five cases, the pseudopentosans are less digested than the residue, and the residue more so than the total crude fiber, although the difference is not great. The digestibility of the residual nitrogen-free extract has been placed in the table for purposes of comparison. With timothy hay, and crabgrass hay, it is less digestible than the residual crude fiber, in one case more, the other two less, digestible than the pseudopentosans. With the green rape, its digestibility is slightly greater than that of the residual crude fiber. With the starchy foods, its digestibility is greater, as a matter of course, since it consists for the most part of starch.

#### COMPOSITION AND DIGESTIBILITY OF CRUDE FIBER.

	In 100 parts		Digestibility.		Residual nitrogen-free extract	
	Pseudo-pentosans.	Residue.	Total.	Pseudo-pentosans.	Residue.	free extract
Timothy hay No. 1 .....	9.2	90.8	52.3	46.9	53.3	50.1
Timothy hay No. 2 .....	14.4	85.6	53.8	52.0	54.1	46.0
Crabgrass hay No. 1 .....	13.0	87.0	67.3	69.9	67.0	32.7
Crabgrass hay No. 2 ....	13.4	86.6	....	62.5 <sup>2</sup>	....	....
Cowpea-meal <sup>3</sup> .....	0	100.0	39.2	....	39.2	97.4
Corn bran <sup>1</sup> .....	0	100.0	50.8	....	50.8	86.1
Green rape No. 1 .....	7.7	92.3	90.0	84.6	90.4	91.4
Green rape No. 2 .....	6.3	93.7	84.0	75.9	84.6	86.5
Rice bran <sup>1</sup> .....	8.3	91.6	19.1	....	19.1	85.0

While, therefore, the order in the series, sugar, starch, pentosans, and residual nitrogen-free extract, is subject to little doubt,

<sup>1</sup> J König: *Landw. Versuch. Stats.*, 48, 93.

<sup>2</sup> Calculated from ration with crabgrass hay.

<sup>3</sup> Calculated from ration with cowpea-meal.

## DIGESTIBILITY OF FEEDING-STUFFS.

and the order, residual crude fiber, pseudopentosans, is doubtful, the combination of the two series is more doubtful. The approximate arrangement in the order of digestibility would be sugar, starch, pentosans, residual crude fiber, residual nitrogen-free extract, pseudopentosans, the position of residual crude fiber and pseudopentosans being subject to change.

It is seen that the residual nitrogen-free extract, in three hours at least, is less digestible than the residual crude fiber. Is this an actual or an apparent difference? It is assumed in digestion experiments that those fodder groups which are not digested pass through unchanged, an assumption that must be modified for the nitrogenous matters and the ether extract, since products of metabolism appear in the excrement which fall into these groups. It is quite possible that crude fiber undergoes such a change that renders it soluble in acids or alkalies.

Crude fiber may disappear :

- (1) By formation of soluble compounds and resorption ;
- (2) By decomposition to carbon dioxide and marsh gas ;
- (3) By decomposition with the formation of carbon dioxide and marsh gas, and soluble products which are resorbed ;
- (4) By decomposition with formation of products which are not resorbed, and are soluble in hot acids or alkalies, hence go into the nitrogen-free extract.

Besides the sugars, starches, gums, etc., the nitrogen-free extract of hays is composed of the less resistant portions of cell walls, partly made up of pentosans. Our digestion experiments seem to show that the older and more resistant cell structures (crude fiber) are in many cases digested to a greater extent than the younger and less resistant. To avoid this difficulty, it has been assumed that the more resistant portions are converted by bacteria into gases and soluble products, which are resorbed. This may be part of the truth, but not all of it. It would naturally suppose the less resistant portions—in the nitrogen-free extract—to be attacked by the bacteria first, and the crude fiber ought to be digested more completely than the crude fiber. The explanation that seems probable is, that the crude fiber and undigested nitrogen-free extract, remain several days in the intestines under very favorable conditions for the action of micro-organisms, are decomposed, with formation

of gases, of soluble products which are resorbed, and of insoluble products which pass into the excrement, and, being soluble in acids or alkalies, appear in the analysis as nitrogen-free extract. The digestibility of the nitrogen-free extract would appear less than it really is, and that of the crude fiber, greater.

#### ANALYSIS OF FEEDING-STUFFS.

This work has shown that if we take the sugars, starch, and pentosans from the nitrogen-free extract, the residue is sometimes more, sometimes less digestible than the crude fiber, and often the difference is not great. For this reason, in the analysis of feeding-stuffs, it is of more importance to determine sugar, starch, and pentosan, than to determine crude fiber.

E. Schulze<sup>1</sup> has proposed that, in addition to the determination of crude fiber, the non-nitrogenous matters insoluble in ether, alcohol, water, and diastase solution be determined. The residue would consist of the material of cell walls, insoluble proteids, and a portion of the ash. It is corrected for the ash and proteids. This method should not be used in digestion work, since insoluble nitrogen-free extract or crude fiber may have become soluble during its several days' stay in the animal. It may be used when a knowledge of the properties of a feeding-stuff is desired quickly.

#### SUMMARY.

1. Sugars are found in all feeding-stuffs, are completely digested, as a rule, and their determination is of especial importance in the case of hays and cottonseed-meal.

2. The average digestibility of pentosans in thirty-four samples is 64.2. The average for timothy hay (eight samples) is 53.9.

3. The constituents of the nitrogen-free extract may be arranged in the following order according to their digestibility: (1) sugars, (2) starch, (3) pentosans, (4) residue.

4. The pseudopentosans of crude fiber are less digestible than the residue. The residue is sometimes more, sometimes less digested than the residual nitrogen-free extract.

5. Crude fiber may be changed during digestion so as to appear as nitrogen-free extract in the excrement.

6. The determination of sugar, starch, and pentosans is more important than that of crude fiber.

May, 1900.

<sup>1</sup> *Landw. Versuch-Stats.*, 49, 434.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF  
APPLIED SCIENCE, No. 34.]

## ON THE HYDROCARBONS IN HEAVY TEXAS PETROLEUM.<sup>1</sup>

BY CHARLES F. MABERY AND D. M. BUCK.

Received June 15, 1900.

THE heavy petroleums that hitherto have been looked on as only fit for fuel are capable, if properly refined, of yielding valuable products. This is especially true of the deposits recently exploited in Wyoming, Texas, and in other sections. The Corsicana oil in Texas has been shown by Mr. Clifford Richardson to yield an oil that may be refined into gasoline, burning oil, and other products ordinarily obtained from light petroleums. Large areas of oil territory have recently been developed in Texas that yield oils of higher specific gravity, and that are of value for what they contain of the higher products. The rapid development of Texas oil territory bids fair to advance the state into an equivalent place with California as oil-producing territory.

As to the hydrocarbons which compose the heavy Texas oil, nothing whatever has hitherto been known. It is practically impossible to separate any of its constituents by the ordinary method of distillation. This examination of the Texas oil was undertaken with the purpose of ascertaining the principal series of hydrocarbons which compose the crude oil.

The specimen was obtained from a large territory owned by the Forward Reduction Company, of this city. The crude oil was very thick and dark in color. Its specific gravity at 20° was 0.9500. A determination of sulphur by the Carius method gave 0.94 per cent. These heavy oils almost invariably contain water suspended, and it is almost impossible to remove the water by drying, and the oil can not be distilled while it contains water on account of violent bumping. Under atmospheric pressure, scarcely any of the oil distilled below 240°. After drying by standing a long time in a warm place with fused calcium chloride, when distilled in vacuo under 13 mm. pressure, the distillates collected in the following proportions and gave the specific gravity annexed:

<sup>1</sup> The work in this paper was the subject of a thesis by Mr. Buck for the degree of Bachelor of Science.

150°	150°-230°	230°-300°	Above 300°
10 per cent.	32 per cent.	21 per cent.	37 per cent.
0.8753	0.9222	0.9602	Very thick.

Next 500 grams were distilled under 25 mm. up to 310°, leaving a residue in the flask of 175 grams. The distillations were repeated several times until larger quantities collected at the following temperatures :

125°-130°	140°-145°	160°-165°	175°-180°	195°-200°	215°-220°
0.8744	0.8848	0.8986	0.9095	0.9231	0.9373
	225°-230°	240°-245°	270°-275°		
	0.9432	0.9478	0.9559.		

For the removal of benzene hydrocarbons and other impurities, the constituents with lower boiling-points were treated several times with fuming sulphuric acid, then washed with sodium hydroxide and water. The remaining oil was nearly colorless. In order to prevent decomposition of the less stable constituents with higher boiling-points by the fuming acid, the heavy oil was dissolved in light gasoline. After the solution became colorless, the gasoline was distilled off, leaving the heavy oil. By this method, it is possible to purify any of the distillates with high boiling-points without decomposition.

The fraction 125°-130° (25 mm.), after treatment with the fuming acid, gave as its specific gravity 0.8711, very little less than the specific gravity of the unpurified distillate, indicating that very little else was contained in this fraction but the principal hydrocarbon. A determination of the molecular weight of the oil at the freezing-point of benzene gave 196; required for  $C_{14}H_{26}$ , 194. The index of refraction was also determined and the molecular refraction calculated from it was 62.39; required for  $C_{14}H_{26}$ , 62.34. A combustion of the oil gave 86.56 per cent. of carbon, and 13.46 per cent. of hydrogen; required for  $C_{14}H_{26}$ , carbon 86.59, hydrogen 13.41.

The fraction 140°-145° (25 mm.) was purified in the same manner, and the same determinations were made. The results of the determinations of carbon and hydrogen, molecular weight determinations and molecular refraction led to the formula of the hydrocarbon  $C_{15}H_{28}$ .



By the same method of purification, the fraction  $160^{\circ}$ – $170^{\circ}$  (25 mm.) was obtained nearly colorless, and it then gave as specific gravity 0.8894, only slightly less than the specific gravity of the unpurified oil. Determinations of carbon and hydrogen, of its molecular weight and molecular refraction, gave results leading to the formula  $C_{16}H_{26}$ .

After treatment with the fuming acid, the fraction  $175^{\circ}$ – $185^{\circ}$  (25 mm.) gave as its specific gravity 0.8966, essentially the same as that of the unpurified oil. The formula established by the same determinations as the others was  $C_{17}H_{28}$ .

The specific gravity of the fraction  $195^{\circ}$ – $200^{\circ}$  (25 mm.), after purification with fuming sulphuric acid, was 0.9070. Determinations of carbon and hydrogen, and molecular weight, led to the formula  $C_{18}H_{30}$ , although the low percentage of hydrogen indicated that the distillate contained some of the hydrocarbon with less hydrogen. The distillate  $215^{\circ}$ – $220^{\circ}$  (25 mm.) gave as specific gravity, after purification, 0.9163. Its formula, established by analysis and determination of molecular weights, was  $C_{21}H_{38}$ .

The fraction  $240^{\circ}$ – $245^{\circ}$  (25 mm.) gave as its specific gravity 0.9306. No other determinations were made of this oil than molecular weight, which corresponded to the formula  $C_{22}H_{40}$ . The fraction  $270^{\circ}$ – $275^{\circ}$  (25 mm.) was extremely viscous, and could be purified only by dissolving in gasoline. It gave a clear slightly yellow oil, with a specific gravity 0.9410, practically the same as the unpurified distillate. Determinations of carbon and hydrogen, of molecular weight and molecular refraction, corresponded to the formula  $C_{25}H_{46}$ .

It appears, therefore, that this heavy Texas oil contains hydrocarbons from  $C_{14}H_{26}$  to  $C_{25}H_{46}$  of the series  $C_nH_{2n-6}$ , and higher hydrocarbons  $C_{21}H_{38}$  to  $C_{25}H_{46}$  of the series  $C_nH_{2n-4}$ . From the slight changes in specific gravity after thorough agitation with fuming sulphuric acid, it appears that these condensed methylenes constitute the chief body of the crude oil which distills within these limits. The first series is satisfied by assuming that the molecule is composed of two methylene rings connected in the same manner as diphenyl, with a sufficient number of methyl side-chains to account for the formula or with connecting carbon atoms between the rings. The study of the constituent

of Texas, California, and Canadian petroleum, with high boiling-points, is now in progress.

A summary of the results obtained in the examination of this petroleum is given in the following table :

	B. P. (25 mm.)	Sp. gr.	Index of refraction.	Molecular refraction	
				Calculated.	Found.
$C_{14}H_{28}$	125°-130°	0.8711	1.4713	62.34	62.39
$C_{15}H_{28}$	140°-145°	0.8788	1.4746	66.94	66.70
$C_{16}H_{30}$	160°-165°	0.8894	1.4672	71.55	69.40
$C_{17}H_{34}$	175°-180°	0.8966	1.4721	76.14	73.85
$C_{19}H_{38}$	195°-200°	0.9020	1.4928	85.35	84.70
$C_{21}H_{42}$	215°-220°	0.9163	1.4979	92.46	92.91
$C_{25}H_{50}$	270°-275°	0.9410	1.5152	110.87	111.00

[CONTRIBUTION FROM THE LABORATORY OF HYGIENE, UNIVERSITY OF PENNSYLVANIA.]

## AN EXPERIMENTAL STUDY OF THE GAS-PRODUCING POWER OF BACILLUS COLI COMMUNIS UNDER DIFFERENT CONDITIONS OF ENVIRONMENT.

BY MARY ENGLE PENNINGTON AND GEORGE C. KÜSEL.

Received June 29, 1900.

THE power which some bacteria possess of liberating certain gaseous elements and compounds from suitable culture media has been the subject of a number of investigations. These investigations have brought to light many interesting facts, and have established methods of diagnostic value based upon gas production. Dr. Theobald Smith, in the account of his now classic experiments upon fermentation, has given a number of species which produce gases, the necessary conditions, quantity of gas produced, etc. Various analyses are on record, also, of the gas liberated, these analyses being more or less detailed depending upon the point of view of the investigator and the time when the work was done. Among the earlier workers we find, generally, that they were content with the determination of the amount of carbon dioxide. The residual gas, being found to be explosive, was accepted as hydrogen.

Later studies have been made with more care, and in consequence the presence of other gases has been recognized. Pammel and Bennett<sup>1</sup> have studied the action of several gas-producing organisms with especial attention to their behavior toward

<sup>1</sup> This Journal, 18, 157 (1896).

different sugars; namely, glucose, cane-sugar, and lactose. They mention the fact that the first portions of escaping gas are nearly pure hydrogen, but are inclined to ascribe this to the absorptive power for carbon dioxide possessed by the medium. The culture period for each experiment is given, and the analytical data obtained by growing the organisms in various media, are compared, but nothing further regarding the progressive alteration in the composition of the gas formed is noted.

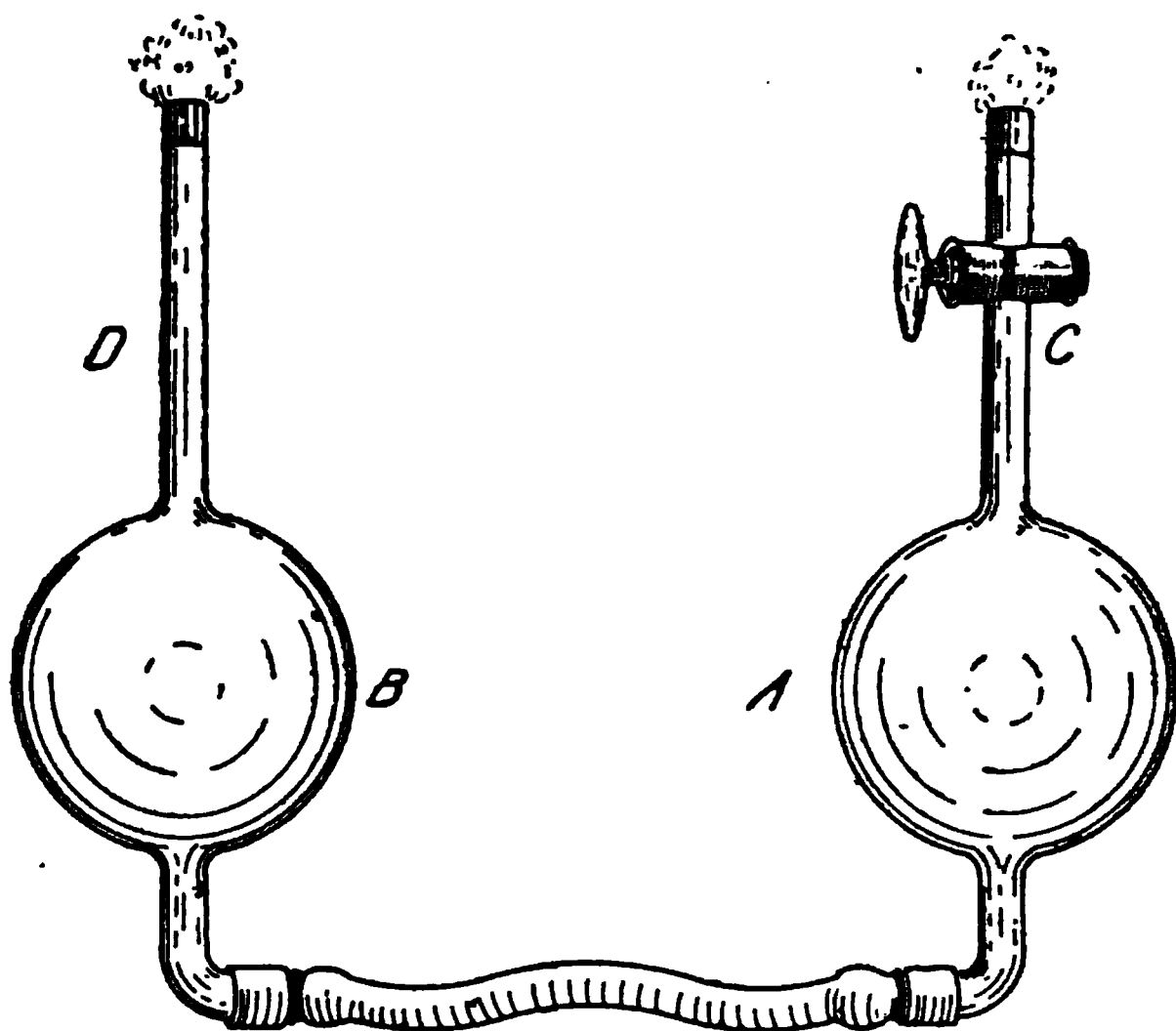
Some fermentation work with *Bacillus coli communis* which has been done in this laboratory, led us to believe that a change in the composition of the gas does occur with the advancing age of the culture and, also, that appreciable quantities of gases other than hydrogen and carbon dioxide are formed. The work in this laboratory also indicated that gas production by *Bacillus coli communis* in glucose bouillon in the usual saccharimeter tube is not so constant, either in relation to time of gas production or of the amount produced, as is generally believed. It seemed advisable, therefore, to cultivate this organism under the most concordant conditions possible, and to submit the gases produced to a careful chemical examination.

The chemist who undertakes quantitative chemico-bacteriological work has found in the past, and still finds, a source of error which at present seems insurmountable. This error lies in the quantity and quality of the inoculating material. Wherever inoculations are to be made the most careful work of trained eyes and skilled hands may yet leave a margin, plus or minus, of untold thousands of organisms, for with cells so prolific as are bacteria a small difference to-day is enormous to-morrow. Not only, too, must we consider the number of active organisms produced, but the waste products of those cells which are already dead may exert an appreciable influence upon later comers.

The gas-producing ability certainly varies considerably with the age of the culture. Many trials have demonstrated that *Bacillus coli communis* made upon nutrient agar are most active so far as gas production is concerned, when three days old, the organisms having been kept at a temperature of 37° C. Older cultures, as a rule, produce less gas. This may be due to a decreased vitality of the germ from lack of food supply or from noxious waste products. In all of the experimental work given

below a three days' slant culture on agar was used as the seeding material.

After many trials with the various forms of apparatus for the collection and isolation of the gases generated by bacteria the following method was devised and used exclusively. The advantage of this form of apparatus is that it is easily handled, cleaned, and sterilized, besides being perfectly tight. That it is



exceedingly simple will be seen from the accompanying diagram. *A* is a glass bulb of 250 cc. capacity having an inlet, *C*, three inches long, into which a glass stop-cock is fused and an outlet *D*, of the same length, bent at right angles about one inch below the bulb. *B* is a like bulb except that the stop-cock is omitted. Heavy walled rubber tubing connects these two bulbs and is closely wired, both outlets being roughened to facilitate this. The inlets are plugged with cotton-wool, when the apparatus may be sterilized in an autoclave.

In the experiments to be described exactly 250 cc. of the desired culture medium were admitted through *D* the stop-cock of *C* being open. The level was then adjusted until the bore of the stop-cock was just filled. The cock was turned, and the apparatus, so far as *A* was concerned, was tight. Resterilization

in an autoclave at 45 pounds' pressure rendered the apparatus fit for inoculation. This was performed either by slipping a platinum wire through the stop-cock bore until it met the medium, or, as we preferred, by placing a definite number of drops of a suspension culture in the inlet tube *C* and drawing them into the bulb by lowering *B*.

As the organisms multiply, the gas collects in *A* displacing the liquid and forcing it over into *B*. The flexible connection between the two bulbs enables one to readily adjust the levels so that undue pressure, which checks fermentation, is obviated. The bulbs have been allowed to stand for days with bulb *B* depressed to its fullest extent but not the slightest inward leakage has been detected. When the experiments were being conducted a slight pressure in *A* was maintained as an additional precaution, so that the leak, if any, should be outward.

All the experiments were conducted at an incubator temperature, 37° C. The media were made with the greatest exactness possible. Commercial peptone, glucose, and salt were carefully dried and weighed accurately. When bouillon was desired Liebig's "*Extractum Carnis*" was used. The reaction of the medium was always neutral at the beginning of the experiment. Tenth-normal sodium hydroxide was used for this neutralization, phenolphthalein being the indicator. The gases were withdrawn from the bulb after cooling the latter to 18° to 19° C. and analyzed over mercury in a Hempel apparatus. Hydrogen was determined by explosion with oxygen. Hydrocarbons were determined by residual carbon dioxide. Nitrogen was found by difference. Heavy hydrocarbons were sought, but were not detected. All results are expressed in percentages. The amount of gas produced did not, as a rule, permit of more than one accurate carbon dioxide analysis. After absorbing the carbon dioxide, however, duplicate determinations of hydrogen, nitrogen, and methane were made. To exclude the personal error all the analyses were made by one person. When the variation in the results were large the experiments were submitted to a bacteriological investigation, but the cultures were found to be pure.

#### NITROGEN AND METHANE.

A series of bulbs were filled as above described with neutral

bouillon containing 1 per cent. peptone, 0.5 per cent. sodium chloride, 0.5 per cent. Liebig's beef extract, and 1.5 per cent. glucose. The individual bulbs were analyzed at the expiration of the periods indicated in the table.

TABLE I.

*Series 1.*

No.	Duration of experiments. Hours.	Carbon. dioxide. Per cent.	Hydrogen. Per cent.	Methane. Per cent.	Nitrogen. Per cent.	Total volume. cc.
1....	72	26.6	65.3	4.30	3.8	93
2....	72	26.45	65.82	3.61	4.12	64
3....	144	28.48	65.83	1.13	4.56	80
4....	168	23.75	70.13	1.15	4.97	67.8
5....	192	23.59	69.88	2.38	4.95	85

*Series 2.*

1....	36	34.30	63.20	1.00	1.30	82
2....	60	33.83	62.69	1.86	1.62	93.4
3....	84	27.03	69.88	1.02	2.07	83

*Series 3.*

1....	48	34.00	63.00	1.5	1.5	93
2....	72	27.5	66.3	3.00	3.2	98
3....	120	28.00	66.5	2.00	3.5	90

According to Table I, in addition to the carbon dioxide and hydrogen, the gases usually present, we find also nitrogen and methane. These gases were invariably found, and their presence in such appreciable quantities is of interest. Grimbert<sup>1</sup> has cultivated *Bacillus coli communis* in the presence of amido bodies, nitrates and nitrites, and states that amides are necessary if denitrification processes are to continue. In Grimbert's experiments sugar was not mentioned, the study being made in nitrated, or amidated, peptone solutions exclusively. In Bennett and Pammel's work we find no mention of nitrogen or methane in the gas produced. Wolff,<sup>2</sup> in a recent paper on denitrification, states that this organism reduces a nitrated peptone—glucose medium, giving nitrites.

Frequent repetition of our experiments, where no nitrates were added, with every possible precaution against admixture of air, gave invariably some nitrogen. The question therefore arose: Does the presence of air in bulb *B* affect the nitrogen production?

<sup>1</sup> *Ann. d. l'Inst., Pasteur*, 13, 67 (1889).

<sup>2</sup> *Hygien. Rundsch.*, 9, 1169.

While fermentation is active the tendency would be to carry the organisms out of the field of activity (bulb *A*) and a backward migration cannot be very extensive. But at the close of the active period the organisms in *B*, may find their way into *A* again. Do they, from their contact with the oxygen at the surface of the liquid in *B*, become so modified physiologically that they alter the usual course of fermentation? To determine this point the following experiments were made in which all oxygen was excluded.

The apparatus above described was filled and sterilized in the usual manner. A Geissler potash bulb containing a freshly prepared pyrogallol and sodium hydroxide solution was attached to *B*, and a wash-bottle rigged flask, containing a like solution, was attached to *A*; the stop-cock was then opened, the level of *A* raised and the liquid allowed to flow into *B*, until the bulb was quite full. The air entering *A* was, of course, deprived of oxygen by the pyrogallate in the wash-bottle flask. The relative levels were next altered and bulb *A* refilled. The air in *B* was free from oxygen and remained so as indicated by testing over active phosphorus. The gas produced under such conditions still showed nitrogen, but we were surprised to find that hydrocarbons had disappeared (see Table II).

TABLE II.

*Series 1.*

No.	Duration of experiment. Hours.	Carbon dioxide. Per cent.	Hydrogen. Per cent.	Methane. Per cent.	Nitrogen. Per cent.	Total volume. cc.
1.....	40	30.00	67.80	.....	2.20	82.0
2.....	64	28.91	67.53	.....	3.56	83.0
3.....	86	28.00	66.99	.....	5.01	83.2

*Series 2.*

1.....	22	34.70	63.58	.....	1.72	83
2.....	36	36.80	60.10	.....	3.10	97
3.....	64	36.00	59.18	.....	4.82	94

Series 1 and 2 of Table II were made with glucose bouillon of the composition given, and, except that the series were started on different days, were as exactly alike as possible. The results show well the marked variation which frequently appears, and which will be again met with in the course of this paper.

Control bulbs without the pyrogallate tubes were made in each case, and the analyses always showed hydrocarbons to be present. Hence we find that the entire exclusion of oxygen does not modify the nitrogen production in the least but that under such circumstances hydrocarbons are not produced.

In the foregoing experiments the organisms had a large supply of amido nitrogen on hand in the form of meat extractives. They had, also, the proteid nitrogen of the peptone. Commercial peptone varies considerably in composition and contains always more or less amido nitrogen. If the organisms are able to reduce the nitrogen of the extractives only we would expect to find much less nitrogen in a peptone-glucose solution than in one containing meat extractives in addition to the other constituents.

To determine to what extent these added meat extractives enter into the nitrogen evolved, the following series of bulbs were made with a culture medium composed of 1 per cent. peptone (Witte's) containing 1.5 per cent. glucose and 0.5 per cent. salt. The pyrogallate bulbs were not attached.

TABLE III.

*Series 1.*

No.	Duration of experiment. Hours.	Carbon. dioxide. Per cent.	Hydrogen. Per cent.	Methane. Per cent.	Nitrogen. Per cent.	Total volume. cc.
1....	24	34.80	65.11	....	0.09	100.0
2....	48	30.2	62.83	1.63	5.34	97.4
3....	120	28.11	64.6	1.80	5.49	86.0

*Series 2.*

1....	46	35.58	60.34	1.34	2.74	97.8
2....	84	32.00	61.39	1.00	4.54	94.8
3....	140	30.00	62.72	1.78	5.50	98.0
4....	144	30.41	62.88	1.77	4.94	96.0

Bulb No. 1 of Series 1, Table II, is the only experiment in which we have failed to detect nitrogen in appreciable amounts. It will be noticed that this bulb also lacks methane. The experiment was carried out in strict accord with the other members of the series, the medium being the same preparation, the inoculation from the same suspension culture. The reason for this variation is unexplained.



**Plate II.**

## Plate III.

A comparison of the nitrogen obtained with and without the addition of extractives shows no appreciable nitrogen difference. If the amido nitrogen only is liberated we have in bulb 4 of Series 2 a quantity of nitrogen corresponding to 0.0184 gram of creatine. According to Allen,<sup>1</sup> Liebig's *Extractum Carnis* contains 29.32 per cent. meat bases. As 5 grams of the extract were added to 1 liter of the medium we have about 1.46 gram of extractives; or, as each bulb was supplied with 250 cc. of the fluid, 0.366 gram was available in each experiment. A very small quantity of amido nitrogen then is split off.

Because of the variability of peptones of different makes another sample, one obtained from Merck, was subjected to experiment.

<sup>1</sup> "Commercial Organic Analysis," Vol. IV, p. 311.

After careful drying it was made into a 1 per cent. solution containing salt and glucose as before. As in the similar experiments with Witte's peptone, extractives were omitted.

TABLE IV.

*Series 1.*

No.	Duration of experiment. Hours.	Carbon dioxide. Per cent.	Hydrogen. Per cent.	Methane. Per cent.	Nitrogen. Per cent.	Total volume. cc.
1.....	24	33.41	64.07	...	2.52	52.0
2.....	48	25.77	64.98	2.00	7.25	50.0
3.....	72	24.16	68.60	2.18	5.06	57.0
4.....	120	24.89	67.36	2.35	5.40	53.0

*Series 2.*

1.....	46	31.80	62.33	1.93	3.94	47.6
2.....	84	31.06	60.33	2.77	5.84	93.6
3.....	140	23.15	67.69	2.60	6.56	50.0
4.....	164	22.69	69.10	3.10	5.11	57.6

With this sample of peptone there was a marked fall in the amount of gas produced, only about one-half the usual quantity being obtained. Bulb 1, of Series 1, Table IV, had made no methane at the end of twenty-four hours, but at the expiration of forty-eight hours, 2 per cent. was present in No. 2. The amount of carbon dioxide is distinctly less than that usually found.

## VARIATION IN AMOUNT OF GASES PRODUCED.

A study of the results which have been obtained discloses an interesting relation from the standpoint of time variation. Table I, Series 1, 2, and 3, were made under conditions as concordant as possible and should therefore be comparable. Uniting these three tables into one we get the following :

TABLE V.

No.	Duration of experiment. Hours.	Carbon dioxide. Per cent.	Hydrogen. Per cent.	Methane. Per cent.	Nitrogen. Per cent.	Total volume. cc.
1.....	36	34.50	63.20	1.00	1.30	82.0
2.....	48	34.00	63.00	1.5	1.50	93.0
3.....	60	33.83	62.69	1.86	1.62	93.4
4.....	72	26.6	65.3	4.30	3.80	98.0
5.....	72	27.5	66.3	3.00	3.20	98.0
6.....	72	26.45	65.82	3.61	4.12	64.0
7.....	84	27.03	69.88	1.02	2.07	83.0
8.....	120	28.00	66.5	2.00	3.05	90.0
9.....	144	28.48	75.83	1.13	4.56	80.0
10.....	168	23.75	70.13	1.15	4.97	67.0
11.....	192	23.59	69.88	2.38	4.95	65.0

There is here a marked difference in the quantitative relations of the various gases according, apparently, to the age of the culture. Charting these results, Plate I, we get a curve which at the end of thirty-six hours shows a maximum quantity of carbon dioxide. Seventy-two hours shows a decrease in carbon dioxide with a corresponding gain in hydrogen. During both of these periods the nitrogen and methane increase slowly but steadily, and are about equal in amount, the only exception being No. 5, eighty-four hours, in which there is a marked absence of both these gases. The third period is marked by a second rise in the amount of carbon dioxide, which is, however, slight, the hydrogen remaining about stationary. The methane now falls behind but the nitrogen is increased, an increase which is maintained in the last period, though here the carbon dioxide is reduced to a minimum and the hydrogen rises to a maximum.

Uniting the series under Table III, and Table IV, we get Tables VI and VII (Plate II and III), where we find that the same principle holds good, though the length of time occupied by the different stages is not exactly the same in all cases.

TABLE VI.

No.	Duration of experiment. Hours.	Carbon dioxide. Per cent.	Hydrogen. Per cent.	Methane. Per cent.	Nitrogen. Per cent.	Total volume. cc.
1.....	24	34.80	65.11	....	0.09	100.0
2.....	46	35.58	60.34	1.34	2.74	97.8
3.....	48	30.2	62.83	1.63	5.34	97.4
4.....	84	32.27	61.39	1.80	4.54	94.8
5.....	120	28.11	64.6	1.80	5.49	86.8
6.....	140	30.00	62.72	1.78	5.50	98.0
7.....	144	30.41	62.88	1.77	4.94	96.0

TABLE VII.

No.	Duration of experiment. Hours.	Carbon dioxide. Per cent.	Hydrogen. Per cent.	Methane. Per cent.	Nitrogen. Per cent.	Total volume. cc.
1.....	24	33.41	64.07	....	2.52	52.2
2.....	46	31.80	62.33	1.93	3.94	47.6
3.....	48	25.77	64.98	2.00	7.25	50.00
4.....	72	24.16	68.60	2.18	5.06	57.00
5.....	84	31.06	60.33	2.77	5.84	39.6
6.....	120	24.89	67.36	2.35	5.40	53.00
7.....	140	23.15	67.69	2.60	6.56	50.00
8.....	164	22.69	69.10	3.10	5.11	57.6

There seems to be, on the whole, an intimate relation between the reducing power which liberates hydrogen and that which liberates nitrogen. Carbon dioxide is generated in greatest quantity at the outset, when, perhaps, the available oxygen is most plentiful and poisonous waste products are in smallest proportion. The reducing power gains strength in the latter stages, when the conditions for carbon dioxide production are not favorable. If, as some investigators maintain, the denitrifying ability of *Bacillus coli communis* is due to a secondary action rather than to a primary one, the rise in carbon dioxide after gas production has been maintained for some hours may be accounted for on the supposition that those substances produced by the organism which liberate nitrogen have, through the reaction involved in that liberation, been so altered that their toxicity for the bacteria is, in part at least, removed. The carbon dioxide function then asserts itself, producing again products which are hurtful. These, combined with those already present, resolutely check the liberation of carbon dioxide. The hydrogen-producing function, as well as the nitrogen, can still maintain its existence for a time, thereby raising the relative proportions of those gases.

We believe that the irregularity of the foregoing results, even when made with the greatest care that we could bestow, is worthy of consideration. For the very great majority of these variations we can offer no definite explanations. It seems to us that refinement in manipulation brings to view variations which can only be due to life conditions, to cope with which our methods are incalculably clumsy. Until these methods are improved the quantitative chemistry of the living cell cannot progress very far, and it is with the plea for further work along these lines that this communication is made.

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## THE ADULTERATION AND ANALYSIS OF THE ARSENICAL INSECTICIDES.

BY J. K. HAYWOOD.

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**I**N the following paper I will first give a résumé of what has been done in the analysis of insecticides, showing which are usually pure and which often adulterated, and laying particular stress on the arsenical insecticides, which are of the most importance now on the market. This will be followed by a series of carefully-tested methods for the analysis of the more common insecticides, with the results indicated.

Various groups of insects act harmfully on plants and require special methods of treatment to kill them. Among these classes of insects may be mentioned subterranean insects, household pests, animal parasites, internal feeders, etc. The insects which principally injure plants, however, and for which insecticides are usually applied, are external feeders, which include "biting" and "sucking" insects.

For the first, or "biting" insects, some substance is used which can be sprayed on the parts of the tree attacked, and then eaten by the insect with its food. Such substances are Paris green, Scheele green, London purple, lead arsenate and arsenite, barium arsenite, arsenious oxide, etc.

For the second group, or "sucking" insects, substances must be used which will act externally on the bodies of the insects and smother them either by closing their pores or filling the air around with poisonous vapors. Among the latter insecticides may be mentioned insect powder, sulphur, kerosene, hydrocyanic acid, carbon disulphide, ammonia, formalin, etc. Experience has proved that a great many of the insecticides mentioned above are nearly always pure as they occur in commerce. There are certain ones, however, which often show adulteration, among them being cupric carbonate (impure because of faulty methods of manufacture), potassium cyanide, potash lye (which is often sodium hydroxide), formalin (which should be a 40 per cent. solution of formaldehyde, but often is not), and most of the arsenical preparations.

I will not attempt to go into the adulteration of all the articles mentioned above, but will lay particular stress on the adulteration of the arsenicals. These include Paris green, Scheele green, London purple, arsenious oxide, lead arsenate, white arsenoid, pink arsenoid, green arsenoid, paragrene, etc.

Paris green is supposed to be copper acetoarsenite and to contain 31.29 per cent. copper oxide, 58.65 per cent. arsenious oxide, and 10.06 per cent. acetic acid.

Scheele green is supposed to be copper hydrogen-arsenite and to contain 42.37 per cent. copper oxide, 52.32 per cent. arsenious oxide, and 4.81 per cent. water.

London purple is a by-product in the manufacture of the aniline dyes and is thought to be composed mainly of calcium arsenite with some coloring impurity, mostly rosaniline arsenite.

Besides London purple there are two other preparations, Paris and English purple, which have practically the same composition.

Of course arsenious oxide should be nearly pure, but in the crude state it may contain from 8 to 10 per cent. of cinders and other impurities.

White arsenoid is supposed to be barium arsenite; pink arsenoid is supposed to be lead arsenite; and green arsenoid is supposed to be copper arsenite.

Paragrene is a patented article which is said to be free from the objectionable features of Paris green, in that it never scorches the foliage.

Excepting the arsenious oxide, all of the above preparations may be, and often are, adulterated in one of three ways:

1. Some colored substance may be used to represent the compound, which will contain none of the elements which should be in the true compound. For example, samples have been analyzed which were labeled Paris green, but which contained neither arsenious oxide nor copper. Such imitations are usually harmless to the plant, but are equally harmless to the insect. Such a fraud as the above was noticed at the Alabama Station,<sup>1</sup> where a sample, called Paris green, was found to be composed of Prussian blue, chrome-yellow, and some inert substance, such as clay or chalk.

<sup>1</sup> Bulletin No. 58.

2. Some substance or substances may be added to the insecticides to increase their weight or to change their color, for use in making pigments. For example, Paris green is often adulterated with calcium sulphate, calcium carbonate, lead chromate, etc. This second form of adulteration is practiced more often in Germany than in America.

3. There may be arsenical insecticides containing a low per cent. of arsenious oxide in combination. It will be noticed that I say in combination. Many of the insecticides contain enough arsenic to include them in the class of high-grade articles, but this arsenic is often not in combination as it should be, but present as free arsenious oxide, thus forming a substance which will scorch the foliage of the tree.

The last of these three forms of adulteration is the most common in America, and must be considered as a fraud when we remember that free arsenious oxide not only scorches the foliage, but is usually much cheaper than the compound, which ought to be present. Sometimes it appears that the free arsenious oxide is added purposely; sometimes it is free because of faulty methods of manufacture.

Paris green, or copper acetoarsenite, has been repeatedly analyzed at the New Jersey Agricultural Experiment Station,<sup>1</sup> and has been found to range in percentage of arsenious oxide from 41.54 to 68.59 per cent. The excessively high percentage of arsenious oxide indicates that this cheaper substance had been added to the Paris green. Again, a sample of Paris green has been recently analyzed at the California Agricultural Experiment Station,<sup>2</sup> which contained 31.25 per cent. copper oxide and 52.90 per cent. arsenious oxide, but 23.60 per cent. of arsenious oxide, or nearly one-half, was in the free state. There were, besides, small amounts of impurities, including lime, soda, silica, sulphur trioxide, zinc oxide, etc. This most likely represents a sample where faulty methods of manufacture were used.

Another sample of Paris green, analyzed at the New Hampshire Station,<sup>3</sup> was found to have the following composition:

<sup>1</sup> Report, 1897. pages 397-492.

<sup>2</sup> Bulletin No. 126.

<sup>3</sup> Bulletin No. 43.



	Per cent.
Arsenious oxide (does not say whether free or combined) ..	30.00
Insoluble in hydrochloric acid .....	43.30

This insoluble portion was composed mainly of silica and oxides of iron and alumina, thus indicating that clay was the adulterant used.

Again at the Massachusetts Hatch Experiment Station,<sup>1</sup> two samples of so-called pure Paris greens were analyzed, which, not including various small amounts of impurities, had the following compositions :

	Per cent.	Per cent.
Water at 100° .....	5.00	4.29
Arsenious oxide .....	58.44	63.98
Copper oxide .....	8.30	6.60
Calcium oxide .....	14.50	15.98
Sulphur trioxide .....	7.56	5.80

The above analyses, of course, show adulteration with calcium sulphate. Samples of Paris green analyzed in Germany have been found to contain calcium sulphate, barium sulphate, lead chromate, lead sulphate, calcium carbonate, etc. One especially contained 25 per cent. of barium sulphate and 6.56 per cent. of lead chromate.<sup>2</sup>

As to Scheele green, the same adulterants are found as in Paris green. In a sample which I have just analyzed, the arsenious oxide and copper oxide appear in nearly theoretical proportions, but 17 per cent. of the arsenious oxide is in the free condition, thus making the sample worthless, unless previously treated with lime.

As to London purple, a sample analyzed at the New Jersey Station showed the following composition :

	Per cent.
Water .....	3.27
Arsenious oxide .....	41.44
Calcium oxide .....	24.32
Alumina and iron .....	3.37
Sulphur trioxide .....	0.31
Dye by difference .....	27.97

The arsenic in this sample was found to be present in the form  $\text{Ca}_3(\text{AsO}_3)_2$ , or the normal arsenite, but about 15 per cent.

<sup>1</sup> Bulletin No. 38.

<sup>2</sup> Stillman: *Chem. News*, 80, Nos. 20,087 and 20,088.

was soluble ; therefore, although this sample was not adulterated, the analysis shows very careless making, as the manufacturers could just as easily have boiled with enough lime in the beginning. The process of manufacture, by the way, is to boil a waste product consisting of dye and arsenious oxide with lime, to make the insoluble calcium arsenite. Samples of London purple have been analyzed at the Cornell Station,<sup>1</sup> South Carolina Station,<sup>2</sup> the Florida Station,<sup>3</sup> and elsewhere, and wherever soluble arsenious oxide was determined it was found to be present in large amounts. It will also be easily seen that, owing to the intense color of London purple, various substances might be added to increase the weight without being perceptible to the naked eye.

White arsenoid, which is supposed to be barium arsenite, has recently been analyzed at the California Station<sup>4</sup> and found to possess the following composition :

	Per cent.
Barium carbonate.....	44.05
Barium chloride.....	13.05
Barium oxide.....	8.18
Arsenious oxide, free.....	27.64
Lead carbonate.....	1.86
Silica .....	0.20
Water .....	4.00

It will be seen that the only substance giving to this preparation any value as an insecticide is arsenious oxide, and since this is in the free state, it is harmful to the foliage. The barium salts are present only to give weight.

Pink arsenoid is supposed to be lead arsenite. A recent analysis made at the California Agricultural Experiment Station<sup>4</sup> showed that it had the following composition :

	Per cent.
Lead oxide.....	49.58
Arsenious oxide, combined.....	40.02
Arsenious oxide, free .....	3.24
Water .....	0.31
Organic matter from aniline residue and lead sulphate....	6.85

<sup>1</sup> Bulletin No. 18.

<sup>2</sup> S. C. Report, 1888, page 142.

<sup>3</sup> Florida Station Bulletin No. 14.

<sup>4</sup> Bulletin No. 126.

This preparation is evidently unadulterated and has given very good results.

Green arsenoid, or copper arsenite, analyzed at the California Station,<sup>1</sup> showed the following composition :

	Per cent.
Arsenious oxide .....	61.33
Copper oxide .....	28.83
Water .....	2.77
Silica .....	0.40
Organic material, sodium sulphate, etc. ....	6.67

7.82 per cent. of this arsenious oxide was soluble.

Paragrene has also recently been analyzed at the California Station and found to owe its poisonous properties mainly to arsenious acid and copper oxide. It contains 23.46 per cent. copper oxide and 40.60 per cent. of arsenious oxide, but 23.08 per cent. of this is free. It also contains 19.31 per cent. of gypsum to add weight. The preparation is therefore harmful to the plant.

In the Canada Experimental Farm Report of 1895, page 220, mention is made of lead arsenate. This substance is obtained by the action of sodium arsenate on lead acetate. It is there stated that there is no reason lead arsenate so manufactured should contain impurities, but that it often does, however, because of the original impurities in the sodium acetate, a by-product obtained in the manufacture of aniline dyes.

Arsenious oxide, because of its method of preparation, may, in the crude state, contain from 2 to 10 per cent. of arsenious sulphide and ore dust as impurities, it being usually prepared by roasting mispickel or tin ores.

I must not leave this subject without calling attention to two insecticides, called respectively " Peroxide of Silicates " and " Hammond's Slug Shot." The first, on analysis at the Vermont Station,<sup>2</sup> was shown to have the following composition :

	Per cent.
Water .....	1.44
Arsenious oxide .....	1.47
Copper oxide .....	0.28
Lime .....	36.43
Sulphur trioxide .....	52.29
Ferric oxide and aluminum oxide .....	1.40
Sand .....	1.93
Organic and volatile matter .....	4.76

<sup>1</sup> Bulletin No. 126.

<sup>2</sup> Bulletin No. 12.

It is needless to say that this sample, composed mostly of calcium sulphate, did not give good results.

"Hammond's Slug Shot," by an analysis made at the Vermont Experiment Station,<sup>1</sup> was shown to have the following composition :

	Per cent.
Water of hydration .....	14.76
Arsenious oxide.....	1.58
Cupric oxide .....	0.60
Lime .....	30.24
Sulphur trioxide.....	43.02
Ferric oxide and aluminum oxide.....	0.79
Sodium chloride.....	2.83
Insoluble.....	1.38
Organic and volatile matter (mostly dead oil by difference).....	4.79

Here again it will be seen that in buying the above substance one is paying a pretty good price for an article composed almost entirely of calcium sulphate.

I have gathered together a bibliography of the arsenical insecticides, of which the examples presented above form only a small fraction. These are, however, fairly representative of the different classes of adulterants.

#### ANALYSIS OF INSECTICIDES.

(Paris green and Scheele green.)

Recently it became necessary for me to make analyses of various arsenical insecticides, but on looking up the matter I found that few good methods had been published. Many of the Stations had partially analyzed these substances, but even the methods employed in these partial analyses were not given. I therefore decided to test some of the few more promising methods which are known, and where methods were not known, try to work them out on the following substances : Paris green, Scheele green, London purple, and white arsenic.

An analysis of Paris green would include determinations of total and soluble arsenious oxide, copper oxide, moisture, acetic acid, and matter insoluble in dilute hydrochloric acid. An analysis of Scheele green would include determinations of all the substances named above, except acetic acid. An analysis

<sup>1</sup> Bulletin No. 12.

of white arsenic would, of course, include only the determinations of water and total arsenious oxide to ascertain the purity.

A determination of the moisture in Paris green is made in the usual way by drying for twelve to fifteen hours, at the temperature of boiling water. On two samples the results were :

	A. Per cent.	B. Per cent.
Moisture .....	1.30	0.99

1. For a determination of the total arsenious oxide, I first tried the well-known method, as given by Fresenius, of dissolving in hydrochloric acid, oxidizing to arsenic acid with potassium chlorate, driving off the chlorine at a gentle heat, making ammoniacal, precipitating with magnesia mixture, filtering and washing in a Gooch crucible, putting a cap on the crucible drying first at  $100^{\circ}$  and then at  $130^{\circ}$  C., heating on a sand-bath, then on an iron plate, and finally heating over the blast-lamp and weighing as magnesium pyroarsenate. This method, however, in the first place, is very long because of the time taken in getting rid of the chlorine and in igniting the precipitate by degrees; secondly, there is great danger of loss of the arsenic, as arsenious chloride; and thirdly, the precipitate of ammonium magnesium arsenate is somewhat soluble in the ammonia wash and has not quite the theoretical composition. After obtaining rather varying results, this method was abandoned.

2. I next tried to determine the arsenic by the following method: Oxidize the Paris green in a small flask, closed with a funnel on the steam-bath, by means of fuming nitric acid. Pour out in a dish and evaporate to dryness; take up with hydrochloric acid and proceed as in the first method, finally weighing the arsenic as magnesium pyroarsenate. This plan shortens the time necessary to determine the arsenic and rids one of the danger of loss as arsenious chloride, but there is still present the third source of error, mentioned above. Proceeding in this way, I obtained the following results on two samples of Paris green ("A and B"), and on a sample of dry, chemically pure arsenious oxide:<sup>1</sup>

<sup>1</sup> In every case where the arsenic was weighed as magnesium pyroarsenate, a correction was made of 0.0008 gram magnesium pyroarsenate, for each 30 cc. of ammoniacal filtrate containing an excess of magnesium mixture as suggested by Fresenius.

	Arsenious oxide. Per cent.
Paris green, "A".....	{ 56.03 56.03
Paris green, "B".....	{ 56.68 56.69
Arsenious oxide, C. P .....	{ 99.33 99.18

3. I next tried a method suggested by Thorn Smith.<sup>1</sup> As described by himself, the method is as follows :

" Two grams of Paris green are weighed out and about 100 cc. of water and 2 grams of sodium hydroxide added. The solution is brought to a boil and the boiling is continued for a few minutes (thus precipitating copper as cuprous oxide). It is then allowed to cool to room temperature and the solution made to 250 cc. The well-shaken liquid is filtered through a dry filter and 50 cc. taken for analysis. This portion is concentrated to about one-half of its volume and allowed to cool to about 80°C. An equal volume of strong hydrochloric acid is then added, accompanied by 3 grams of potassium iodide, and the whole allowed to stand for ten minutes (to reduce the arsenic oxide to arsenious oxide). The deep red solution is slightly diluted with water to dissolve the precipitate caused by the potassium iodide, and a dilute solution of sodium hyposulphite added, until the color just disappears. This solution is then made neutral by the addition of dry sodium carbonate and finally an excess of sodium bicarbonate is added. Tenth normal iodine is dropped in and the end reaction noted by the starch solution."

In applying this method, I used one or two precautions, not mentioned by Smith ; namely, instead of making neutral with dry sodium carbonate and very likely getting in an excess, I added dry sodium carbonate until the bubbles came off slowly, showing that the acid was really neutralized, and then sodium bicarbonate to neutrality and some in excess. This was done, because if any free sodium carbonate is present it will itself act on the iodine solution. Again, after using up the iodine which was set free in reducing the arsenic to arsenious oxide by sodium hyposulphite, the solution was immediately diluted, since the air

<sup>1</sup> This Journal, 21, 769.

is apt to act on the hot, concentrated solution of hydriodic acid and set free some iodine if this is not done.<sup>1</sup>

On applying this method to the two samples of Paris green ("A" and "B") and the dry, chemically pure arsenious oxide the following results were obtained :

	Arsenious oxide. Per cent.
Paris green "A" .....	{ 56.85 56.96
Paris green "B" .....	{ 57.63 57.45
Arsenious oxide, C. P. <sup>2</sup> .....	{ 100.10 100.10 99.86

It will not be out of place here to speak of the standardization of the iodine solution, since it is upon the correctness of this standardization that the accuracy of the above method depends. A great many text-books give the following method for standardizing the iodine solution :

Weigh out a small portion of dry, chemically pure arsenious oxide, dissolve in sodium hydroxide, make slightly acid with hydrochloric acid, and then add an excess of sodium bicarbonate. Run in the iodine solution, using starch as an indicator, until the blue color appears.

I used this method of standardizing at first, but it soon seemed to me that perhaps it was not correct, since the literature on the subject speaks of the alkali arsenites being partially oxidized to the "arsenates" upon boiling the solution, exposed to the air. I therefore used a dry, chemically pure portion of arsenious oxide and carried it through by the Thorn Smith method, standardizing my iodine solution against the arsenious oxide, as finally reduced by potassium iodide. In every case, I found that on adding potassium iodide to the hydrochloric acid solution of the arsenite some iodine was set free, showing that a small amount of arsenate had been formed, which should be reduced before running in the iodine solution.

Applying these two methods to an approximately tenth-normal

<sup>1</sup> Gooch and Browning : *Am. J. Sci.*, 40, 66 (1890).

<sup>2</sup> The iodine solution for the determination of arsenic trioxide in the chemically pure arsenic trioxide was not standardized against arsenious oxide, but against sodium hyposulphite, which had in turn been standardized against the amount of iodine set free, when potassium iodide acts on a weighed quantity of potassium dichromate in the presence of hydrochloric acid.

iodine solution, I obtained by the old method of standardization 1 cc. iodine solution = 0.012607 gram iodine, and by the Smith method of standardization 1 cc. iodine solution = 0.012484 gram iodine. It will at once be seen that the errors caused by the sodium arsenite partially oxidizing to sodium arsenate is larger than should be allowed in a standard solution.

A determination of the copper oxide in Paris green was made in the following well-known manner:

The cuprous oxide obtained in the Thorn Smith method by boiling the Paris green with sodium hydroxide was poured on the filter (after taking an aliquot portion of the solution for the determination of arsenious oxide) and well washed with hot water. It was then dissolved with hot dilute nitric acid and made to a volume of 250 cc., one-fifth being taken for analysis. The copper in solution was determined either by means of the galvanic current or, when that was not handy, in the following manner:

The nitric acid solution was made alkaline with sodium carbonate, then made slightly acid with acetic acid, and about ten times the weight of the copper in potassium iodide added. When it was all dissolved, the free iodine was titrated with a standard solution of sodium hyposulphite, using starch as indicator. The full details of this method are given in Sutton's "Volumetric Analysis," third edition, page 133. The results on the two samples of Paris green by this method were as follows:

	Cupric oxide. Per cent.
Paris green "A".....	{ 29.79 30.37 30.15
Paris green "B" .....	{ 29.79 29.79 29.79

The figure for acetic acid in Paris green is usually obtained by subtracting the sum of total arsenious oxide, water, cupric oxide, and residue left after treating with dilute hydrochloric acid, from 100.

As to the determination of soluble arsenic in Paris green, I could find very little in the literature on the subject which was of any value. I therefore tried several schemes:



1. I weighed 1 gram of Paris green on a filter-paper and washed it with cold water. Each time 200 cc. were obtained, sodium bicarbonate was added and the solution titrated with iodine solution. After about 2,000 cc. of wash liquor had been used the filtrate was still slowly gaining in arsenious oxide. The method was therefore abandoned as impracticable.

2. I weighed out several 1-gram samples of Paris green and treated these in flasks with 500 cc. of water. The flasks were stoppered and occasionally shaken each day. Every few days an aliquot portion of 100 cc. was filtered off from one of the flasks and the arsenious oxide titrated with iodine after the addition of sodium bicarbonate. The results on the samples of Paris green ("A" and "B") were as follows:

	Time. Days.	Arsenious oxide extracted. Per cent.
Paris green "A".....	2	1.01
" " ".....	4	1.68
" " ".....	8	2.69
" " ".....	11	4.02
" " ".....	14	4.02
" " "B".....	9	3.41
" " ".....	12	4.86
" " ".....	14	4.86

It will thus be seen that this method finally gave constant and very likely correct results. It is rather long, but very little attention or time had to be given after the first weighing out.

3. To expedite matters, I next tried the following method for determining the soluble arsenious oxide. One-half gram of Paris green was weighed out, placed in a flask and treated with about 200 cc. of water. This was digested with occasional shaking on the water-bath at 50° to 60° C., and each day all of the water poured off through a filter, and, after returning all of the substance from the filter to the flask, a fresh portion of water was added and the digestion continued. The arsenious oxide was determined by means of a standard iodine solution. The results on the samples of Paris green ("A" and "B") were as follows:

	Time. Days.	Arsenious oxide extracted. Per cent.
Paris green "A".....	1	3.41
" " ".....	2	3.41 + 2.14 = 5.55
" " ".....	3	5.55 + 1.56 = 7.11
" " ".....	4	7.11 + 1.17 = 8.28
" " ".....	5	8.28 + 1.26 = 9.54
" " ".....	6	9.54 + 1.56 = 11.10
" " ".....	7	Still gaining.
" " "B".....	1	2.24
" " ".....	2	2.24 + 1.46 = 3.70
" " ".....	3	3.70 + 1.26 = 4.96
" " ".....	4	4.96 + 1.17 = 6.13
" " ".....	5	6.13 + 1.17 = 7.30
" " ".....	6	7.30 + 1.56 = 8.86
" " ".....	7	Still gaining.

It will thus be seen that a hot extraction can not be used, since the Paris green either breaks up or goes into solution in the presence of hot water, the amount of arsenious oxide going into solution each day being finally nearly constant.

The same methods for determining the constituents of Scheele green were used as those for Paris green mentioned above. On one sample the moisture was 5.27 per cent.

The total arsenious oxide was as follows :

By Method 1. Oxidation with HCl and KClO <sub>3</sub> .....	Not tried
By Method 2. Oxidation with HNO <sub>3</sub> .....	{ 50.63 50.80
By Method 3. Thorn Smith.....	{ 51.39 51.27

The determination of the cupric oxide by the method mentioned above gave the following results :

Cupric oxide .....	{ 38.04 38.23
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The soluble arsenious oxide determination gave the following results by the various methods :

- 1. Washing on filter. Not tried.
- 2. Extracting with 500 cc. cold water :

Time. Days.	Arsenious oxide extracted. Per cent.
6 .....	13.09
9 .....	14.30
13 .....	16.26
21 .....	16.73
34 .....	17.82
36 .....	17.70

3. Extracting with water at 50° to 60° C.:

Time. Days.	Arsenious oxide extracted. Per cent.
1 .....	13.43
2 .....	13.43 + 3.70 = 17.13
3 .....	17.13 + 1.85 = 18.98
4 .....	18.98 + 0.87 = 19.85
5 .....	19.85 + 0.78 = 20.63
6 .....	20.63 + 0.58 = 21.21
7 .....	21.21 + 0.49 = 21.70
8 .....	21.70 + 0.39 = 22.09
9 .....	22.09 + 0.39 = 22.48
10 .....	22.48 + 0.39 = 22.87
11 .....	Still gaining.

From the above work I would draw the following conclusions :

- 1. Water can be determined in Paris green and Scheele green by drying at the temperature of boiling water for twelve to fifteen hours.
- 2. The best method for determining the total arsenious oxide in Paris and Scheele greens is the Thorn Smith method, marked 3 above.
- 3. The best method for determining the soluble arsenious oxide in Paris and Scheele greens is by extracting with 500 cc. of water at room temperature.
- 4. Hot water extraction can not be used to extract soluble arsenious oxide.
- 5. A good method for determining copper in Paris and Scheele greens is the volumetric method based on the titration of the iodine set free from potassium iodide by a copper salt in acetic acid solution.

Appended is a condensed statement of the work done :

		Total arsenic.		
	Water. Per cent.	Oxidation with potas- sium chlorate.	Oxidation with nitric acid.	Method of Smith.
			Per cent.	Per cent.
Paris green "A" .....	1.30	Abandoned	56.03	56.90
Paris green "B" .....	0.99	"	56.69	57.54
Scheele green .....	5.27	"	50.66	51.33
Arsenious oxide, C. P.	None	"	99.25	100.02

	Soluble arsenious oxide.			Cupric oxide. Per cent.	Insoluble in hydrochloric acid.
	Wash on filter.	500 cc. cold water. Per cent.	Water at 50°-60° C.		
Paris green "A".....	Abandoned	4.02	11.10+	30.07	None
Paris green "B".....	"	4.86	8.86+	29.79	None
Scheele green.....	"	17.76	22.87+	38.14	None
Arsenious oxide, C. P.	....	....	....	....	None

A continuation of this paper will appear during the next few months, which will have for its object the creation and improvement of the methods of estimating the various constituents of London purple as well as a study of the improved method of estimating arsenic gravimetrically by Martha Austin,<sup>1</sup> which has only come to my notice since the above work was completed.

## THE DETECTION OF COAL-TAR DYES IN FRUIT PRODUCTS.

BY A. L. WINTON.

Received July 5, 1900.

SOON after its discovery fuchsine came into use for coloring wines and replaced to a large extent the vegetable dyes which from very early times had been employed for this purpose. More recently various other coal-tar dyes, particularly the azo-colors, have been extensively used in wines although fuchsine and acid fuchsine are still preferred by some makers.

Within the past few years the use of coal-tar dyes in articles of diet has attracted the attention of food analysts in the United States. In the case of confectionery, pastries, and some other products they serve merely to render the articles more attractive to the eye without deceiving the purchaser, but as a rule they give imitation products the appearance of the genuine or, to use the legal phraseology, "they make the products appear better or of greater value than they really are."

Some of the results obtained by Winton, Ogden, and Mitchell, in the examination of foods at the Connecticut Agricultural Experiment Station, illustrate the fraudulent use of dyes. In 1898, sixty-three samples of jellies purporting to have been made from fruit were examined, and of these, twenty-eight were spurious mixtures colored with coal-tar dyes. Some of the most remarkable samples, labeled "strawberry jelly," "raspberry

<sup>1</sup> *Ztschr. anal. Chem.*, 23, heft 2.

jelly," etc., consisted of starch paste, flavored with artificial "fruit ethers," sweetened with glucose and preserved with salicylic acid, the dye having been used to carry out the deception. Of twenty-eight samples of fruit preserves, eight were also colored with coal-tar dyes. During the following year (1899) ninety-two samples of soda-water sirups, chiefly strawberry, raspberry, and orange, were subjected to analysis. Of these, forty-five were colored with coal-tar dyes. As a rule the sirups which were artificially colored were also artificially flavored and contained no genuine fruit juice whatever. Dyes were also found in bottled carbonated beverages.

The relation of these dyes to public health deserves attention. The experiments carried on with dogs and other animals by Cazeneuve and Lépine, Weyl, and others have proved beyond a doubt the poisonous nature of picric acid, dinitrocresol, and Martius' yellow, among the nitro-colors, and of orange II and metanil yellow among the azo-colors. Fuchsine, sulphonated nitro-colors, and most of the azo-colors did not act as poisons although some of the azo-colors produced vomiting, others diarrhea, and many developed slight albuminuria.<sup>1</sup>

Although there is evidence that the bulk of the coal-tar dyes are not injurious to some of the lower animals, it is not safe to assume that they are entirely harmless to human beings. The dog, the animal used in most of Weyl's experiments, has a proverbially strong stomach and eats, with no apparent discomfort, many things which would disturb the digestion of a man.

The unwholesomeness of certain coal-tar dyes not classed as poisons is indicated by the experience of Weber<sup>2</sup> who tested their effect on the artificial digestion of fibrin with pepsin and with pancreatin. He found that oroline yellow (acid yellow) retarded the action of pepsin and that methyl orange, saffoline (acridine red), and magenta (fuchsine) seriously interfered with the pancreatic digestion. Of these, fuchsine, at least when pure, had been pronounced entirely harmless by earlier investigators who based their conclusions on experiments with lower animals and some few with man.

<sup>1</sup> "The Coal-tar Colors" by Theodore Weyl, translated by Henry Leffmann, pp. 54-148.

<sup>2</sup> This Journal, 18, 1092.

Even if the entire harmlessness of most of the coal-tar dyes is conceded, in view of the injurious properties of some of them and the difficulty of distinguishing these from the harmless dyes when present in food products, the safe course is to exclude all dyes of coal-tar origin from articles of diet. In Austria their use is entirely prohibited and in other countries they are regarded with suspicion.

In carrying out the work of food examination under adulteration laws the analyst is often called upon to determine whether or not a coal-tar dye is present, if not to identify the particular dye.

Numerous methods of testing wines for these dyes are described in the journals and in the works on food analysis but almost nothing has been published on their detection in jellies, preserves, fruit sirups, and other fruit products.

Because of the absence of special methods I have adapted some methods originally devised for wines for use in testing other products and publish the following details, with precautions learned by experience, for the benefit of others engaged in similar work.

In applying these tests to jellies and other semisolid products it is necessary to bring into solution by boiling with 1 to 5 parts of water.

#### ARATA'S WOOL TEST.<sup>1</sup>

One hundred cc. of the liquid to be tested, prepared if necessary as described in the preceding paragraph, are boiled for ten minutes with 10 cc. of 10 per cent. solution of potassium bisulphate and a piece of white wool, or woollen cloth, which has been previously heated to boiling in a very dilute solution of sodium hydroxide and thoroughly washed in water. After removal from the solution, the wool is again washed in boiling water and dried between pieces of filter-paper. If the coloring-matters are entirely from fruit, the wool either remains uncolored, or takes on a faint pink or a brown color which is changed to green by ammonia and is not restored by washing in water; but if certain coal-tar dyes, chiefly of the azo-group, are present,

<sup>1</sup> *Ztschr. anal. Chem.* 28, 639. See also Borgman: "Anleitung chem. Anal. d. Weines," Wiesbaden, 1898, p. 91. Koenig: "Untersuchung landw. u. gewerb. wich. Stoffe." Berlin, 1898, 577.

the wool is dyed and the color on the fibers is either not changed by ammonia or, if changed, is restored by washing.

The dye present may often be identified by noting the color of the wool after addition of enough concentrated sulphuric acid to thoroughly moisten the fibers and again after dilution of the acid.<sup>1</sup> As a rule it is not desirable to proceed further with the test although Arata gives instructions for removing the dye from the wool and testing the dye itself. For this purpose the wool is treated with dilute tartaric acid solution to remove vegetable colors, washed in water and dried between sheets of filter-paper. It is then transferred to a test-tube and saturated with concentrated sulphuric acid. After standing five or ten minutes, water sufficient to make 10 cc. is added and the wool is removed. The solution after making alkaline with ammonia and cooling is shaken with 5 to 10 cc. of pure amyl alcohol, to which a few drops of ethyl alcohol are added, to facilitate the separation. The alcoholic extract is separated, evaporated to dryness, and the residue tested according to the scheme of Girard and Dupré, Witt,<sup>2</sup> Weingaertner<sup>3</sup> or Dommergue.<sup>4</sup>

I have applied this test to samples of juices, sirups, jellies, and preserves prepared in the laboratory from the fruits, as well as to numerous commercial fruit products including catsups. The woolen cloth used was "nun's veiling" cut into pieces one inch wide and three inches long.

When strawberry, raspberry, blackberry, currant, grape, and cherry juices, without dilution, were treated as has been described, the wool acquired a dull pink or brownish pink color. With ammonia the color changed to green, and washing with water in no case restored the original color. Treatment with 10 per cent. tartaric acid solution in the cold was without effect, but on boiling for some time the pink color was largely removed. From orange, lemon, pineapple and tomato juice or pulp, the wool absorbed no color at all, or only a faint yellow color.

Jellies, preserves, sirups, and catsups known to be pure gave up to the wool very slight colors, but many of the commercial

<sup>1</sup> See scheme of Girard et Dupré: "Analyse des Matières Alimentaires et Recherche de leurs Falsifications."

<sup>2</sup> *Ztschr. anal. Chem.*, 26, 100.

<sup>3</sup> *Ibid.*, 27, 232.

<sup>4</sup> *Ibid.*, 29, 369.

products imparted to the wool intense red, orange, magenta, and even green shades. Treated with ammonia, these bright colors remained unchanged or, if changed, washing restored the original color.

Boiling with tartaric acid solution also failed to affect the colors. By treatment with concentrated sulphuric acid and dilution of the acid, color reactions for acid fuchsine, tropæolins, ponceaus, Bordeaux red, eosins, and other dyes were obtained.

I have found it more satisfactory to test the dyed wool directly, rather than the color obtained from the wool as directed by Arata, because only a few dyes are extracted by amyl alcohol from alkaline solutions, and, as explained further on, tests of the residues left after evaporating the extracts are indecisive.

Care should be taken to determine whether the wool is dyed, or merely coated with the color. For example, chlorophyl from green coloring preparations of vegetable origin, is deposited on wool, together with fat and resin, but the color, unlike the coal-tar dyes, rubs off on the fingers and is readily washed out with soap and water.

For the purpose of illustrating the amount of artificial color present in each glass of adulterated carbonated beverages, I have employed 250 cc. portions of the beverages (or 40 to 50 cc. of sirups diluted to 250 cc.) and pieces of nun's veiling six inches square. The dyed squares thus obtained furnish striking object lessons. From strawberry, raspberry, cherry, and blood-orange flavors, brilliant red and magenta shades were fixed on the wool (acid magenta, Bordeaux red, ponceaus, etc.); from orange and lemon flavors, orange and yellow shades (tropæolins, etc.); and from mint preparations, bright green and yellow-green colors.

#### AMYL ALCOHOL TEST, ALKALINE SOLUTION.<sup>1</sup>

Twenty-five cc. of the liquid to be tested, made alkaline with ammonia, are shaken cautiously for some minutes in a separatory funnel, with pure amyl alcohol. If the clear alcoholic layer, when separated from the aqueous solution, is colored, or if addition of acetic acid develops a magenta color (fuchsine), a portion of it, together with an equal bulk of water and a thread of

<sup>1</sup> "Analyse des Matières Alimentaires et Recherche de leur Falsifications", Par Girard et Dupré, pp. 167, 582.



wool, is heated on a water-bath, the water lost by evaporation being replaced from time to time.

The presence of a coal-tar dye should not be affirmed until the color has been fixed on wool and the wool has been washed in boiling water, dried, and tested with sulphuric acid. When fuchsine is present, the color which appears on adding acetic acid to the alcohol extract is changed to yellow by hydrochloric acid. Ether or ethyl acetate may be used in place of amyl alcohol for extracting fuchsine.

#### AMYL ALCOHOL TEST, ACID SOLUTION.<sup>1</sup>

Twenty-five cc. of the liquid, to which have been added a few drops of hydrochloric acid, are shaken with amyl alcohol, and dyeing tests are made as described in the preceding section.

A colored amyl alcohol does not prove the presence of a coal-tar color, as I have found that red coloring-matters are extracted by this solvent from acid solutions of pure fruit juices. These solutions, however, do not dye wool, when treated as above described.

Some authors recommend that the sulphuric acid test be applied to the residue left after evaporating the amyl alcohol extract. This may be satisfactory in wine analysis but with fruit jellies, etc., this residue is liable to contain other organic matters which obscure the color reactions of coal-tar dyes.

If amyl alcohol extracts from the liquid, after acidifying, an orange color which has not been found to be of coal-tar origin, test may be made for cochineal.

The alcohol is washed several times with water and divided into two portions. To one portion is added a solution of uranium acetate, drop by drop, with shaking. In the presence of cochineal the aqueous solution acquires an emerald-green color.<sup>2</sup> As a confirmatory test the other portion is made alkaline with ammonia which changes the orange color of cochineal to purple.

#### GIRARD'S TEST FOR ACID FUCHSINE (ACID MAGENTA).<sup>3</sup>

If a bright magenta color is fixed on wool by Arata's test and

<sup>1</sup> "Analyse des Matières Alimentaires et Recherche der leur Falsifications," Par Girard et Dupré, p. 582.

<sup>2</sup> *Ibid.*, p. 580.

<sup>3</sup> *Ibid.*, p. 169.

if ordinary fuchsine has been proved to be absent, test should be made for acid fuchsine.

To 10 cc. of the liquid are added 2 cc. or more of 5 per cent. solution of potassium hydroxide. The strongly alkaline liquid is mixed with 4 cc. of 10 per cent. solution of mercuric acetate and filtered. The filtrate should be alkaline and colorless. If addition of a slight excess of dilute sulphuric acid produces a violet-red coloration and other dyes have not been found by the amyl alcohol test, the presence of acid fuchsine may be affirmed.

I have found this test useful in the examination of fruit juices and sirups but unsatisfactory in the case of jellies owing to difficulties in filtration and undecisive reactions.

#### CAZENEUVE'S METHOD.

Cazeneuve's mercuric oxide method<sup>1</sup> for detection of coal-tar dyes which has been extensively employed in wine analysis did not prove satisfactory in the examination of jellies. This method, however, deserves trial with fruit juices and sirups, which are more easily handled than the gelatinous products.

In testing a suspected sample I apply first of all Arata's test. The other tests described are employed either to confirm the results obtained by Arata's test or to supply evidence in cases where that test fails.

The analyst should be extremely cautious in naming the particular dye present in a sample. It should be remembered that the number of coal-tar dyes on the market is exceedingly large and that new dyes are continually being introduced. A reaction which a few years ago may have been characteristic of a particular dye may to-day be common to several dyes. As a rule it is only necessary to learn whether or not a color is of coal-tar origin. In fact such terms as "red coal-tar dye" and "orange coal-tar dye" are often to be preferred in an official report to the cumbersome scientific names or the equally unintelligible commercial names.

CONNECTICUT AGRICULTURAL EXPERIMENT STATION,  
NEW HAVEN, CONN., June, 1900.

<sup>1</sup> "Analyse des Matières Alimentaires et Recherche der leur Falsifications," Par Girard et Dupré, p. 174; *Compt. rend.*, 102, 52.

[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION  
OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

## ESTIMATION OF FAT IN CONDENSED MILK.

BY ALBERT E. LEACH.

Received July 9, 1900.

**T**HE use of canned, sugar-preserved, condensed milk has increased considerably during the last few years, no less than forty brands of the article being on sale in Massachusetts at the present time. In view of the fact that of all its ingredients the fat is the only one that can be conveniently tampered with to produce an inferior or cheaper product, it becomes highly important to have at hand a ready and accurate means of fat determination, especially where samples have to be examined systematically and in large numbers for adulteration.

The Babcock centrifuge method, so convenient for estimating fat in ordinary milk, was long thought to be out of the question for use with sugar-preserved milk, by reason of the fact that the cane-sugar, which is present to the extent of some 40 per cent. in the average condensed milk, becomes so charred by the action of the sulphuric acid employed in the test as to produce nothing but a black mass in place of the desired column of clear fat. This has been the common experience of all who tried it.

The Adams-Soxhlet method, which is the recognized standard for fat determination in ordinary milk, has been largely used in the case of condensed milk, but, in the writer's experience, can not be depended on for the latter purpose, on account of the fact that the large amount of cane-sugar present, even when the sample is diluted for analysis, encloses the fat particles so firmly, when dried on the extraction coil, as to render its removal by the solvent ether a very difficult matter.

In 1895 the writer devised a scheme whereby the Babcock machine could be satisfactorily used for condensed milk fat, and an outline of the process as then carried out was published in the "Annual Report of the Massachusetts State Board of Health for 1896." This process, with certain minor modifications which experience has from time to time suggested, has been in successful use in the Food and Drug Department of the Board for over five years, and has proved itself to be not only much quicker

than the Adams-Soxhlet extraction method and easier of manipulation, but, indeed, more accurate, by reason of the fact that the cane-sugar with all its attendant troubles is first eliminated.

If, in the case of condensed milk, ordinary ether is used as a reagent for the Soxhlet extraction, the amount of extract weighed as fat may not *appear* too low, because the alcohol and water present in the ether dissolve not only fat, but also sugar, which goes in with, and is weighed as fat. On the contrary, if the ether be dehydrated with calcium chloride and distilled over sodium, to free it completely from alcohol, the extracted fat will be found to be far too small. The same incomplete extraction results from the use of benzine or petroleum ether as a solvent.

Parallel determinations of fat in sugar-preserved milk by the Adams-Soxhlet process, using ether carefully dehydrated and freed from alcohol, and by the writer's method involving the use of the Babcock machine, show in all cases a larger fat content by the latter or modified Babcock process. Indeed, in one instance an extraction of sixty hours was required in the case of the Soxhlet process to equal the percentage of fat found by the modified Babcock process, so firmly were the fat particles enclosed by the cane-sugar on the extraction coil, thus resisting the action of the ether. It is obvious that, in the case of the modified Babcock process, no more fat can be shown by the final result than actually exists in the milk; indeed, if anything, one would expect a slight loss, so that, when compared with the Soxhlet method, if the latter shows lower figures, it can safely be presumed that the process is unreliable. This, of course, applies only to the sugar-preserved variety of condensed milk.

The improved method of fat estimation with the Babcock centrifuge is as follows: Having first insured a homogeneous sample of the contents of the can by stirring, 40 grams are weighed out preferably in a weighing tray for sugar, transferred by washing to a graduated 100 cc. sugar flask, and made up to the mark with water. Twenty-five cc. of the thoroughly mixed diluted sample, corresponding to 10 grams of the original condensed milk, are measured by a pipette into an ordinary test-bottle of the Babcock centrifuge. This is filled nearly to the neck with water, and 4 cc. of a solution of copper sulphate of the strength of Fehling's copper solution are added. The contents are thor-

oughly shaken, and the precipitated proteids, carrying with them the fat, are rapidly separated out by whirling the fat bottle in the centrifuge, preferably (though not necessarily) without heating. The writer prefers an electric centrifuge of the Robinson type for this purpose, as the heat of the steam-driven machine cakes the precipitate down, so that it is harder to wash. If desired, the precipitate may be allowed to settle out of itself, which it does more quickly in the cold.

The supernatant liquid containing the sugar is drawn off by means of a pipette of large capacity, having a stem sufficiently small to pass easily into the neck of the milk bottle, a small wisp of absorbent cotton being first twisted over the bottom of the pipette to serve as a filter. If many samples are to be treated, a suction-pump, connected by rubber tubing with the pipette, is a great convenience. On withdrawing the pipette with the sugar solution, the cotton is wiped off into the bottle by rubbing against the inner side.

The precipitated proteids and fat are given two additional washings, as above, by shaking thoroughly with water introduced nearly to the neck of the bottle, separating out in each case by centrifuge or by settling, and finally removing the washings with the pipette, two of such extra washings being found nearly always sufficient to remove all the sugar. If the precipitate is caked down hard after treatment with the centrifuge, it may be necessary to employ a stiff platinum wire as a stirrer to aid in mixing with the wash-water.

Finally, enough water is added to amount approximately to the normal volume of 17.6 cc. usually employed for the Babcock test, 17.5 cc. of sulphuric acid are added, and the test continued from this point on as in the ordinary Babcock process of milk testing, multiplying the reading obtained by 1.8 to give the correct percentage of fat in the sample.

For condensed milk containing no added cane-sugar, these precautions are, of course, unnecessary, the ordinary Babcock method being directly employed with a weighed portion of the milk.

# ON CERTAIN PECULIARITIES IN THE URINE OF VEGETARIANS.

BY J. H. LONG.

Received July 23, 1900.

I HAVE recently presented the results of analyses of a number of normal urines<sup>1</sup> in which the relation of the copper oxide reducing power to the amounts of creatinin and uric acid present, was especially noted. In this paper I shall give briefly the corresponding data found by examining the urine of individuals living wholly on a vegetable diet. As the methods of examination were the same as formerly employed, it will not be necessary to refer to them again. The seven men who furnished the urine for the tests are students of the American Medical Missionary College of Battle Creek and Chicago, and for a year or longer had lived on a diet of bread, fruits, vegetables, and prepared cereal and nut foods exclusively. Eggs were not eaten, and only as much milk as was taken with the "cereal coffee" used. The whole day's excretion was furnished me in each case. The table following gives the important data secured as explained in the heading over each column.

No. of sample.	Excretion in twenty-four hours. cc.	Specific gravity at 20°.	Urine required to reduce 50 cc. of copper solution. cc.	Ammonia from 1000 cc. of urine. Mg.	Urea from 1000 cc. of urine by Liebig process. Gms.	Uric acid from 1000 cc. of urine. Mg.	Creatinin from 1000 cc. of urine. Mg.	Chlorine from 1000 cc. of urine. Gms.	P <sub>2</sub> O <sub>5</sub> from 1000 cc. of urine. Gms.
1	800	1.029	16.2	745.0	28.9	668.5	1551.6	6.65	1.89
2	805	1.030	16.3	522.0	28.8	645.0	1288.7	9.66	1.77
3	850	1.030	18.1	431.7	30.6	693.7	556.0	8.44	2.07
4	610	1.031	18.2	607.3	28.5	622.5	87.4	9.15	2.09
5	975	1.032	17.3	944.2	40.7	930.0	958.8	6.60	2.41
6	920	1.031	18.5	854.1	34.7	817.5	1123.7	7.88	2.38
7	494	1.030	16.7	507.7	32.4	765.0	362.8	6.10	1.40
8	1040	1.023	25.7	483.9	27.5	626.2	170.7	6.24	1.81
9	685	1.032	16.5	896.8	36.6	753.7	795.9	6.17	2.40
10	1025	1.029	19.6	982.2	33.8	588.7	847.6	5.75	2.50
11	1065	1.029	21.1	640.5	29.2	746.2	1337.3	....	....
12	850	1.030	19.1	716.5	31.9	810.0	1157.8	....	....

This Journal, 22, 309.

No. of sample.	Excretion in twenty-four hours.	Specific gravity at 20°.	Urine required to reduce 50 cc. of copper solution.	Ammonia from 1000 cc. of urine.	Urea from 1000 cc. of urine by Liebig process.	Uric acid from 1000 cc. of urine.	Creatinin from 1000 cc. of urine.	Chlorine from 1000 cc. of urine.	P <sub>2</sub> O <sub>5</sub> from 1000 cc. of urine.
	cc.		cc.	Mg.	Gm.	Mg.	Mg.	Gm.	Gm.
13	800	1.031	17.1	626.3	34.8	843.7	790.1	....	....
14	1020	1.028	19.2	498.2	28.8	705.0	889.6	....	....
15	850	1.030	20.2	711.7	32.2	952.5	1082.7	9.77	....
16	800	1.030	17.9	1043.9	38.8	731.2	1137.2	....	....
17	950	1.027	22.8	616.8	28.6	656.2	1017.4	8.17	....
18	1020	1.027	22.7	607.3	26.8	645.0	1003.0	10.19	....
19	800	1.031	16.1	683.2	33.2	1166.2	1558.8	7.68	....
20	950	1.031	19.2	1062.8	35.8	843.7	805.7	9.02	....
21	925	1.030	17.3	1262.1	37.1	978.7	1157.8	9.06	....
22	905	1.030	18.4	1072.3	34.2	746.2	1547.0	9.38	....
23	860	1.030	17.2	920.5	41.6	780.0	361.1	....	....
24	970	1.028	21.6	664.3	32.4	705.0	247.5	8.35	1.85
Mean	874	1.030	18.9	754.2	32.8	767.6	909.8	8.01	2.05

At first sight we notice the rather marked reducing powers of these urines which in the mean appears to be about 20 per cent. greater than in the cases described before. But at the same time it will be observed that these urines in general are highly concentrated, the average daily excretion being only 874 cc. as against 1167 cc. for the former series. If weakened then to the same dilution the total copper oxide reducing power, expressed in these terms, would be brought down even lower. In other words, for the daily excretion the reduction is not large. The probable reason for this will be evident from what follows.

Making due allowance for differences in concentration there is nothing noteworthy in the excretion of urea, uric acid, and ammonia, or for chlorine and phosphoric acid found in part of the cases, but for the excretion of creatinin we have remarkably low figures in general. The former investigation gave as the normal relation of uric acid to creatinin about 1 : 2, but here we have about 1 : 1.2. The value for the uric acid excretion is based on a volume of 1000 cc. but if calculated for the volume voided in twenty-four hours, is brought down to 671 milligrams, which is a fair average.

The correspondingly low creatinin points apparently to low metabolism, and is a fact of considerable importance. Creatinin is supposed to reach the urine in one of two ways. Many physiologists (for illustration see Schaefer's "Text-book of Physiology," p. 599) attribute it mainly or wholly to the creatin found in the lean meat consumed as food, and changed by dehydration in the liver, while on the other hand, it may be a product of body muscle metabolism. That it is not necessarily dependent on the creatin of meat has long been recognized by numerous writers since its appearance in urine during starvation has been abundantly demonstrated. The above tests fully confirm this view. The food of the persons furnishing the urines for experiment was certainly free from anything more than traces possibly of either creatin or creatinin, and had been for a period of months or years. Yet we find a creatinin excretion which is within the limits given as normal in many of our text-books. This must be traced to muscular creatin, formed in turn by metabolism of the food proteids. This view is rendered more probable by the discovery pointed out by several recent writers of the close relation of creatin and similar bodies to the derivatives of proteids formed by various hydrolytic cleavages. Although the simple relation suggested by Drechsel<sup>1</sup> in which the resemblance of creatin to lysatin was shown, no longer appears to hold since Hedin and others have made it evident that lysatin is probably a mixture of arginin and lysin,<sup>2</sup> we still have the creatin-like nature of arginin itself as a very interesting fact<sup>3</sup> pointing to the same general relation. The fact that the hexone bases are produced in trypsin digestion as well as by acid hydrolysis<sup>4</sup> has probably no bearing in the case in suggesting another possible source of the creatinin found, besides that of muscle katabolism, as the amounts which may be so formed are usually very small.

That the creatinin was relatively low in all the urines was probably due to low food consumption and metabolism. The men furnishing the urine performed little muscular work and took but little exercise. In a few cases the results were very

<sup>1</sup> *Ber. d. chem. Ges.*, 23, 3096.

<sup>2</sup> *Ztschr. physiol. Chem.*, 21, 297.

<sup>3</sup> Schulze and Winterstein: *Ztschr. physiol. Chem.*, 26, 1.

<sup>4</sup> See papers by Kossel and Mathews and by Kutscher: *Ztschr. physiol. Chem.*, 25, 190 and 195. in illustration.



low ; this can not be explained by accidental error in the experimental methods, concentration of the urine with alkaline reaction, for example, but must depend on some relation not at present discernible. The tests were all carefully made in the same manner and precautions were taken to secure a final concentrated filtrate in which zinc chloride would certainly precipitate any creatinin present.

The distribution of the reducing power in these urines is also interesting. It will not be necessary to make the calculation for each case as was done in the former paper, but the average results may be taken. The table above gives 18.9 cc. of urine in the mean as the volume required to reduce 50 cc. of the standard copper solution containing 2.604 grams of cupric oxide to the liter. From this it may be calculated that 1000 cc. of the urine would reduce 6.888 grams of cupric oxide. This is a high figure because of the marked concentration of most of the urines. Making a similar calculation from the data of the last paper we find that the creatinin of 1000 cc. of the average urine would reduce 1.282 grams of cupric oxide, while the uric acid would reduce 1.091 grams. The sum of these reductions is 2.373 grams, or a trifle over one-third of the total reduction. We have remaining 4.515 grams of cupric oxide per liter as the amount corresponding to the carbohydrates or similar bodies present. In view of the character of the food consumed this is an interesting but not unexpected result. Allowing for the concentration the reduction due to carbohydrates is still large. It is evident, therefore, that a diet wholly vegetable, in which carbohydrates and fats predominate, favors the increase in the non-nitrogenous (probably carbohydrate) factors in the urine. My thanks are due to Mr. Frank Wright and Mr. Charles Erickson for the experimental work.

NORTHWESTERN UNIVERSITY, CHICAGO,  
June 20, 1900.

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## REVIEWS.

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### AN EXPERIMENTAL STUDY OF RADIO-ACTIVE SUBSTANCES.<sup>1</sup>

Professor Röntgen's remarkable discovery, in 1895, of the penetrating rays called by him X-rays, but now equally well known by his own name, was followed in 1896 by Becquerel's announcement that the salts of uranium emit invisible radiations capable of discharging electrified bodies and of producing skiagraphic images on sensitive plates. He found that potassio-uranic sulphate emits rays that pass through black paper and affect photographic plates; this property is not limited to the brilliantly fluorescent uranic salts, but is shared by the non-fluorescent uranous salts. All uranium compounds examined proved to be active, whether phosphorescent or not, whether crystalline, melted or in solution; and metallic uranium exhibits the phenomena in a marked degree. The permanence of this property is amazing, substances kept in a double leaden box more than three years emitted rays having almost as much power as when first tested.

Shortly after the announcement by Becquerel, experimenters found that other substances have the power of emitting these "Becquerel rays;" M. Henry found it in phosphorescent zinc sulphide, Niewenglowski in insolated calcium sulphide, Troost in artificial hexagonal blende, and Schmidt in thorium compounds. In 1898 Mme. Sklodowska Curie, working in the laboratory of the Municipal School of Industrial Physics and Chemistry in Paris, devised a special apparatus for measuring the electrical conductivity of the air when under the influence of "radio-active bodies," and by its means studied the behavior of the minerals pitchblende, chalcocite, autunite, cleveite, monazite, orangeite, and thorite, and found them all active. Some varieties of pitchblende showed more than three times as much energy as metallic uranium itself, and this led her to the conclusion that the peculiar property was due to some unknown body contained in the mineral, and not to uranium compounds. Associating with her, her husband, Mme. and M. Curie attacked the mineral pitchblende with acids and reagents and soon obtained results that were presented by M. Becquerel to the Academy of Sciences, Paris, at a meeting held Monday, 18th July, 1898.

These savants showed that pitchblende contains a substance, apparently analogous to bismuth, which emits Becquerel rays

<sup>1</sup> Read at a meeting of the Chemical Society of Washington, held April 21, 1900, at Baltimore, Md.

4000 times stronger than uranium; they were unable to isolate the element having radiant power but they named it "Polonium," in honor of the native land of Mme. Curie. In December of the same year the lady received the Gegner prize of 4000 francs awarded her by the Academy of Sciences, and later in the same month M. and Mme. Curie, together with M. Bémont (director of the Municipal Laboratory), announced the discovery of a second radio-active body in pitchblende, which they called "Radium." Since that date Mme. Curie and her husband have industriously carried on investigations, publishing their results in the *Comptes rendus*; and some German physicists, not gallant enough to leave the enterprising woman a clear field, have announced some minor discoveries. From these papers we gather the following facts concerning these marvelous bodies.

As yet, comparatively little is known of the chemistry of the salts of polonium, since the radio-active substance has not been separated from its companions; on working up the mineral pitchblende the polonium is found in the precipitate thrown down by hydrogen sulphide, and insoluble in ammonium sulphide. Solutions of polonium react like those of bismuth, being precipitated by water.

The mixture of substances in which radium shows its activity has been more fully studied; the yet unknown element accompanies barium in analytical separations, its chloride is wholly soluble in water, and it responds to the usual tests for barium. The spectrum of the substance shows the bands of barium together with other lines peculiar to radium.<sup>1</sup> Attempts to separate radium from barium have been unsuccessful, but by fractional precipitation of the mixed chlorides with alcohol a salt has been obtained having 900 times the activity of uranium.

By operating on half a ton of the residues of uranium minerals, Mme. Curie obtained 2 kilograms of material rich in radium; with this, attempts were made to determine the atomic weight of radium, and she found the figures 140, the atomic weight of barium being 136.4.

The extraordinary physical properties of the rays emitted by these bodies have commanded the most attention; they possess luminosity, actinic and skiagraphic power, and render the air through which they pass a conductor of electricity. This latter property, the one which led to their discovery, is studied by means of an electroscope of special construction. It consists essentially of a gold-leaf (or aluminium foil) electroscope enclosed in a metallic box with glass sides and communicating with a metal disk exterior to the box. This disk lies in a horizontal plane a few centimeters above another parallel disk which serves as a support for the substances under examination.

<sup>1</sup> Demarcay: *Compt. rend.*, 129, 716, Nov. 6, 1899.

When the electroscope is charged by rubbing the upper disk with a piece of ebonite, the gold-leaf diverges from the perpendicular and will remain so for some time if undisturbed; on placing a layer of any radio-active body on the insulated lower disk the air between the two disks becomes a conductor and the gold-leaf at once resumes its normal position. To estimate the rapidity of the displacement of the gold-leaf, a microscope fitted with a micrometer eye-piece is attached to the apparatus at right angles to the axis, and with the aid of a watch beating seconds the time is noted which the gold-leaf takes to reach a certain point on the scale of the micrometer.

Becquerel first announced that the rays given out by uranium exhibited the phenomena of polarization, reflection, and refraction, but this was not confirmed by other observers and on repeating his experiments with radium and with polonium Becquerel got contradictory and negative results. The French chemist observed that the rays emitted by different bodies are very unequally absorbed; the rays of radium and uranium freely penetrate plates of quartz, fluorite, and mica, but those of polonium are absorbed by these minerals and scarcely penetrate paper. On the other hand rays of polonium pass through aluminium more freely than those of uranium.

The rays of divers origin are also influenced in different ways by a magnetic field; in an irregular magnetic field formed by a powerful electromagnet, the rays emitted by radium are deflected and concentrated on the poles; to show this, Becquerel devised ingenious experiments giving photographic records.<sup>1</sup> On examining the rays of polonium compounds (furnished by Mme. Curie) he found that polonium acted differently from radium,<sup>2</sup> and his results failed to confirm the observations of Geisel previously announced. Later, Mme. Curie also published a note on the dissimilar behavior of the rays of polonium and of radium in a magnetic field.<sup>3</sup> The subject has also been studied at Vienna by Stefan Meyer and Egon R. von Schweidler.<sup>4</sup>

Becquerel rays excite phosphorescence in gems, minerals, barium sulphide, calcium sulphide, etc.; in fluorite the phosphorescence remains twenty-four hours after the influence of radium has been removed, much as when exposed to the light of the electric arc.

In studying the power that these rays have of communicating energy to inactive bodies, Mme. Curie worked with substances so well purified that they were 50,000 times more powerful than uranium, and the induced activity measured 1 to 50 times that

<sup>1</sup> *Compt. rend.*, 130, 996, Dec. 11, 1899.

<sup>2</sup> *Ibid.*, Dec. 26, 1899.

<sup>3</sup> *Ibid.*, 130, 73, Jan. 8, 1900.

<sup>4</sup> *Phys. Ztschr.*, 10, 113.

of uranium; the substances examined were zinc, aluminum, brass-foil, lead, platinum, bismuth, nickel, paper, barium carbonate, and bismuth sulphide. Her experiments showed that a true induction of radiant energy is effected, and the energy imparted to metallic plates is not removed by washing with water although the radium chloride ("chlorure de barium radifère") is soluble. The activity induced by Becquerel rays persists, while that caused by Röntgen rays ceases suddenly on removal of the agent.<sup>1</sup>

The actinic power of the rays is shown by exposing the salts to sensitive plates; with the relatively pure material obtained by Mme. Curie an exposure of one-half minute sufficed to get an impression. The peculiar power of Röntgen rays is seen by using a barium platinocyanide fluoroscope, the rays exciting fluorescence through aluminum, vulcanite, etc.<sup>2</sup>

Mme. Curie records obtaining good "photo-impressions" with uranium, uranous oxide, pitchblende, chalcocite, etc., through glass, air, and aluminum.

The spontaneous luminosity of radium compounds was announced by Mme. Curie to the Physical Society of Paris in March, 1899,<sup>3</sup> and in November of that year she published her discovery that the wonderful rays exert chemical action. They transform oxygen into ozone; this was first noticed by the odor of the air in a flask in which radium compounds were confined, and was confirmed by the usual test with potassium iodide starch-paper. The rays also produce a certain coloration in glass changing it to violet; and they transform barium platinocyanide from yellow to brown, in which state it is less fluorescent, but this can be revived by insolation.<sup>4</sup>

At the suggestion of Mme. and M. Curie, M. A. Debierne, working in the laboratory of the Sorbonne, examined pitchblende for other radio-active bodies, especially the portion precipitated from solution by ammonia and ammonium sulphide, after separation of the uranium; in October, 1899, he found associated with titanium, a substance exhibiting 100,000 times more radiant power than uranium, and having chemical properties distinct from radium and polonium. The rays emitted by this body, named actinium, have the same manifold action as the other substances, with the exception that it is not self-luminous.<sup>5</sup>

In a more recent paper<sup>6</sup> M. Debierne finds that actinium is

<sup>1</sup> *Compt. rend.*, 124, 714, Nov. 6, 1899.

<sup>2</sup> *Ibid.*, 126, 1101 (1898); 127, 1215, Dec. 26, 1898.

<sup>3</sup> *Rev. chim. pure et appliquée*, July, 1899.

<sup>4</sup> *Compt. rend.*, 129, 823 (Nov. 30, 1899).

<sup>5</sup> *Ibid.*, 129, 593.

<sup>6</sup> *Ibid.*, 130 (April 12, 1900).

allied to thorium, and suggests that the radio-activity of the latter is due to admixture of the new substance.

To complete this review of the radio-active bodies, brief notice must be made of two papers by German chemists. Fritz Geisel obtained radium from uranium ores other than pitchblende, and remarks: "Freshly crystallized Ba salts containing Ra are only slightly active, but in a few days or weeks they reach a maximum. They are strongest when anhydrous, moisture stops activity and heating restores it."<sup>1</sup>

Becquerel rays have the same intensity in partial vacuum as at ordinary air-pressure; this was proved by electrical and photographic experiments made by J. Elster and H. Geitel.<sup>2</sup>

Through the enterprise and liberality of the Smithsonian Institution, and by the courtesy of Secretary Langley, I have enjoyed the opportunity of studying small specimens of these rare and costly substances; they comprise 10 grams of "radio-active substances" in two portions, prepared by E. de Haen, manufacturing chemist of Hannover, Germany, and 4 grams of "chlorure de barium radifère," and 4 grams of "polonium sub-nitrate" from the "Société Centrale de Produits Chimiques (Ancienne Maison Rousseau)", Paris, said to be prepared according to the instructions of Mme. and M. Curie.

The samples from Hannover were marked "A" and "B" respectively, and a memorandum accompanying them stated that "B" excites fluorescence in barium platinocyanide more energetically than "A," whereas the latter is self-luminous; as a matter of fact I found both luminous in the dark and "B" the brighter of the two.

The specimens were enclosed in hermetically sealed bottles and protected from light by straw-board cylinders; on removing the wrappings in a dark room both were seen to emit greenish white light that gave to the enveloping papers a peculiar glow, similar to the fluorescence produced by Röntgen rays. I here call especial attention to the fact that during all the time that I have had the substances under examination they have been kept in the dark, no light reaching them stronger than that of the yellow and orange-red of a photographic dark room, so that insolation has played no part in renewing their energy.

The grayish white powders proved to be wholly soluble in water and the solution gave the usual reactions for barium chloride.

Moistening the radium chloride with cold water does not immediately stop emission of light, but on heating to boiling, the luminosity ceases. The water was expelled and the material, heated in a platinum dish to dull redness, resumed its luminosity

<sup>1</sup> *Ann. Phys. Chem.*, 69, 91 (1898).

<sup>2</sup> *Wied. Ann.*, 66, 135 (1898).

after a few days *in the dark*. The fact that radium compounds resume their power of emitting light slowly has been noted by Geisel, but he fails to state whether the salt regains its property without exposure to sunlight.

The substances "A" and "B" were examined with a fluoroscope at first without success, but in a perfectly dark room, after the eyes became sensitive, the screen of barium platinocyanide was distinctly seen to fluoresce feebly.

The small specimens of these bodies had no perceptible influence in exciting phosphorescence of sulphides of the alkaline earths exposed to their action.

Having at hand no apparatus for measuring the electrical conductivity of the air, my experiments were chiefly directed to ascertaining the action of the rays on sensitive plates.

The photographic experiments were made with Seed non-halation dry plates (No. 26). To test the approximate actinic power of the bodies "A" and "B," sections of sensitive plates at distances of 5 and 10 inches were exposed at intervals of from two to twelve minutes; these gave bands varying in intensity with the duration of action. "B" showed far greater power than "A". By exposing sensitive plates behind an ordinary negative to the entire 10 grams of "radium" from two to three hours, good transparencies were obtained; on substituting Eastman's bromide paper, prints were secured; the distance of the sensitive surfaces from the source of light was about 3 inches.

To get skiagraphic images, plates were enveloped in Carbutt's black paper (non-permeable to light) and on this was laid a piece of tin-foil cut in open work pattern; after one hour's exposure a negative was obtained plainly showing the pattern. "A" was apparently stronger than "B".

Analogous experiments were carried out with the specimens of "radium" and of "polonium" from Paris; making allowance for the difference in weight, the radium of German origin was about five times as active as the French. The sample labeled "polonium subnitrate" (weighing 4 grams), had positively no action on the plates used.

Having at my disposal 500 grams exceedingly well purified uranic nitrate (remaining from previous researches), I examined it for Becquerel rays, but a sensitive plate exposed three hours to the beautifully fluorescent crystallized salt gave no trace of action. Similar negative results have been obtained by Sir William Crookes.

The primary source of the energy manifested by these extraordinary substances has greatly puzzled physicists and as yet remains a mystery. Mme. Curie speculating on the matter, at first proposed the following explanation: she conjectured that all space is continually traversed by rays analogous to Röntgen



rays but far more penetrative, and not capable of being absorbed by certain elements of high atomic weight such as uranium and thorium.

Becquerel, reflecting on the marvelous spontaneous emission of light, remarked: if it can be proved that the luminosity causes no loss of energy, the state of the uranium is like that of a magnet which has been produced by an expenditure of energy and retains it indefinitely, maintaining around it a field in which transformation of energy can be effected. But the photographic reductions and the excitation of phosphorescence in a sensitive screen require an expenditure of energy, of which the source can only be in the radio-active substances. As this expenditure is slight perhaps the bodies have a large reserve of energy which can be drawn upon for years without showing loss; at any rate it has been impossible, says Becquerel, to bring about any appreciable variation in the intensity of the emission by physical influences.

Somewhat later Becquerel hazarded the opinion that the radiation of radium is composed at least in part of cathodic rays; but these have been proved to be material, hence the induced activity must be caused by material particles impinging upon the substances excited. This materialistic theory seems to be confirmed by the results of ingenious experiments made by Mme. and M. Curie; they placed a sensitive plate beneath a salt of radium supported upon a slab of lead, in the vicinity of an electromagnet. Under these conditions when the current was passing, the rays emitted by the chemical salt were bent in curved lines upon the sensitive plate, making impressions.

It may be objected, says a French writer in the *Revue générale des Sciences* that this theory requires us to admit actual loss of particles of matter, nevertheless the charges are so feeble that the most intense radiation yet observed would require millions of years for the removal of 1 milligram of substance.

The same writer raises the question, which of the observed phenomena is the primary one? does the radiation of radium excite cathodic rays, or do the latter exist in the chemical compounds? and he regards the latter as improbable. The primordial source of energy in radium probably resides, he adds, in the ultraviolet light, and the efflux of material particles that ensues is only a secondary phenomenon, but on a far larger scale than has previously been observed.

Speculations as to the future history and applications of these wonder-working bodies press upon even the dullest imagination; if a few grams of earth-born material, containing probably only a small percentage of the active body, emit light enough to affect the human eye and a photographic plate, as well as rays



that penetrate with X-ray power, what degree of luminosity, of actinism, and of Röntgenism, is to be expected from an hundred-weight of the quintessence of energy purified from interfering matter?

And to what uses is this light-generating material to be applied? Are our bicycles to be lighted with disks of radium in tiny lanterns? Are these substances to become the cheapest form of light for certain purposes? Are we about to realize the chimerical dream of the alchemists,—lamps giving light perpetually without consumption of oil?

Seriously, in what direction is profound study of these substances going to lead us? Will it not greatly extend our knowledge of physical manifestations of energy and their correlation? What bearing will this power of "opening up paths through the air" for currents of electricity have upon our knowledge of heat, light, electricity, and those forms of energy called by the names of Röntgen and Becquerel?

In what corner of the globe will be found the cheap and convenient supply of raw material yielding the radio-active bodies? Will not chemists be obliged to reexamine much known material by laboratory methods conducted in the dark? Many of us have worked up kilograms of pitchblende to extract uranium oxides and in so doing have poured down the waste-pipe or thrown into the dust-bin the more interesting and precious radio-active bodies.

At all events whatever the future may bring, physicists are deeply indebted to Becquerel, and to Mme. and M. Curie for placing in our hands new methods of research and for furnishing a novel basis for speculations destined to yield abundant fruits.

#### POSTSCRIPT.

Bela von Lengyel, of Budapest, has pointed out that the chemical evidence is insufficient to establish the elementary character of these radio-active bodies, and claims to have prepared the so-called "radium" synthetically. By fusing with the heat of the electric arc uranic nitrate mixed with 2 to 3 per cent. of barium nitrate, and treating the mass with nitric acid, water, and sulphuric acid, successively, he obtained radio-active barium sulphate possessing all the physical properties characteristic of the "element" announced by Mme. Curie. The resulting substance gives out actinic rays, Röntgen rays, excites platino-cyanide screens, and causes air to conduct electricity.

The Hungarian chemist has made and examined the chloride and the carbonate of this substance and finds that they have the same properties; he wishes his paper regarded as a preliminary notice, proposing to continue his researches.

Von Lengyel's paper was received by the German Chemical Society on April 2nd, but the number of the *Berichte*<sup>1</sup> containing it only reached Washington on May 26.

Admitting that radio-active bodies can be manufactured to order, are we any nearer explaining their mysterious powers?

HENRY CARRINGTON BOLTON.

COSMOS CLUB, WASHINGTON, D. C., May 26, 1900.

## MODERN RESEARCHES ON THE CHEMISTRY OF THE PROTEID MOLECULE.<sup>2</sup>

It is impossible, at the present stage of our knowledge, to give any satisfactory definition of a proteid, based either on its physiological or chemical properties. Physiologically, it can be pointed out as the main constituent of all cells and tissues. In regard to its chemical properties, it can be stated with absolute certainty that it consists of carbon, hydrogen, oxygen, nitrogen, and sulphur. It does not possess very marked acid or basic properties, but forms salts with both bases and acids, its affinity for both being very weak.

### I.

It can not be classified under any of the well-established groups of chemical compounds. Some attempts in this direction, however, have been made in recent years; and of these, the attempt to classify all proteids among glucosides has been the cause of much dispute from the experimental and speculative side of the question. The author of this theory and its most enthusiastic advocate was Pavy, who, by hydrolysis of egg albumin, succeeded in obtaining a reducing substance, capable of combining with phenylhydrazine, forming an osozone of a definite melting-point.

Physiologists, who were all inclined to see the source of the tissue-carbohydrates in the tissue-proteids, naturally welcomed Pavy's work, and were ready to endorse his views. A number of researches, however, were undertaken in order to test the correctness of Pavy's statements. The results thereof were contradictory. Morner has investigated, in that direction, serum globulin, and found that on heating with 3-5 per cent. hydrochloric acid, it yielded a solution capable of reducing Fehling's solution. Krawkow has tested, in the same direction, various proteids with different results. Substances combining with phenylhydrazine, giving osozone, were obtained by him from

<sup>1</sup> Vol. 33, p. 1237, May 14, 1900.

<sup>2</sup> Read before the New York Section of the American Chemical Society, May 11, 1900.

egg albumin (m. p.  $183^{\circ}$ – $185^{\circ}$  C.), fibrin (m. p.  $182^{\circ}$ – $184^{\circ}$  C.), and serum albumin (m. p.  $183^{\circ}$ – $185^{\circ}$  C.). He failed to obtain similar substances, or obtained them only in traces from serum globulin, lactalbumin, casein, gelatin, vitellin, and mucoid.

The work which followed that of Krawkow was done by Eichholtz and is instructive in many ways. Thus, in contradiction to Krawkow, he failed to obtain the carbohydrate from serum albumin and succeeded in obtaining it from serum globulin. Of greater interest, however, is the fact that he found in the white of the egg, besides the ovomucoid, a substance related to it, which he called "ovomucin."

In regard to the egg albumin, two other researches are of great importance: first, that of Weydemann, who obtained on treatment of egg albumin with a 10 per cent. solution of sodium hydroxide, a substance similar to "animal gum"; and secondly, the work of Spenser, who repeated, under Drechsel's direction, the experiments of Pavy. Spenser was very careful to remove all the mucoid from the white of the egg, and only used such methods as would exclude the contamination of the egg albumin with the carbohydrates of the filter-paper, etc. Under such conditions, Spenser failed to obtain a carbohydrate on the hydrolysis of egg albumin with acids.

A comparison of the results of all the authors reveals the fact that proteids of the same nature gave different results to different investigators, as can be seen from the following table:

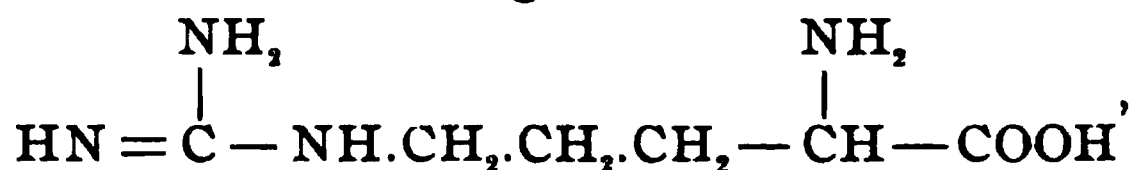
	Pavy.	Krawkow.	Eichholtz.	Morner.	Spenser.
Egg albumin .....	positive	positive	positive	.....	negative
Fibrin .....	"	"	.....	.....	.....
Serum albumin ...	"	"	negative	.....	.....
Serum globulin ...	"	negative	positive	positive	.....
Lactalbumin .....	.....	"	.....	.....	.....
Casein .....	positive	"	.....	.....	.....
Gelatine .....	negative	"	.....	.....	.....
Vitellin .....	positive	"	.....	.....	.....
Mucoid .....	.....	"	.....	.....	.....

Further, new substances related to mucins were discovered where they were not suspected by some of the investigators searching for carbohydrate in the proteid molecule; and finally, those who were more careful in avoiding contamination were the least successful in obtaining the "carbohydrate moiety" of the proteid molecule. It seems therefore unwarranted at the present moment to accept the existence of such a moiety.

## II. THE NITROGEN.

The greatest part of the researches on the chemistry of proteids has been directed to the character and form of the nitrogen present in its molecule. The older authors knew that the nitro-

gen was not all in equally strong combination with the rest of the proteid molecule, and that the nitrogen entered the proteid molecule in the form of an amido group. But of the amido compounds only those of the monamido acids were detected in that molecule. A great part of the nitrogen was in a combination unknown to most of the old investigators. Drechsel was the first to investigate with great success the nature of the nitrogenous residue. He has found that it consists of substances with a well-defined basic nature, some of them being diamido acids. The substances he discovered were lysin and lysatine: one being diamidovalerianic acid,  $C_6H_{14}N_2O_2$ ; the other a homologue of creatine,  $C_6H_{13}N_3O_2$ . Later he also discovered among the decomposition products of proteids diamidoacetic acid. A number of different proteids were examined by the students of Drechsel, namely, E. Fisher, Siegfried, and Hedin, and the presence of the bases lysin and lysatine was demonstrated in all of them. Furthermore, Siegfried isolated besides these two bases, a new one having the composition  $C_{11}H_{20}N_6O_6$ . Hedin then obtained, by the decomposition of different proteids, arginin, a base of the following formula:



and which was first described by E. Schulze as a constituent of vegetating seeds. Later Hedin also demonstrated that the substance, described by Siegfried as  $C_{11}H_{20}N_6O_6$ , was histidin— $C_6H_9N_3O_2$ —a base first discovered by Kossel as a decomposition product of a protamine, "sturin."

The statement of R. Cohn that a pyridin base could be detected among the other basic decomposition products of the proteids was very recently retracted by him.

After the presence of the basic substances in the proteid molecule was demonstrated, the question arose, how are they grouped in the molecule? and the researches of Kossel seemed to fully answer it. Kossel has resumed the work of Miescher on protamines—substances occurring mostly in fish sperm in combination with nucleic acid. The protamines had some properties common with proteids; namely, they gave the same color reaction with an alkaline copper solution as the proteids, a test known as the "Biuret test," undergoing also the same changes in solubility as proteids on digestion with pepsin hydrochloric acid.

Finally they yielded on decomposition the basic substances met with on decomposition of other proteids. The points of difference were that the protamines did not give the other color tests peculiar to proteid material and did not contain the other decom-

position products met with on decomposition of proteids except the "hexon" bases. The conclusion was natural that the property of the proteids to give the biuret test was due to the presence in its molecule of a protamine group. Such actually was the conclusion of Kossel, and, according to his theory, the protamine is the nucleus of all proteids in the same manner as benzene is the nucleus of all the aromatic compounds.

On further investigation, however, it was found that only one protamine, namely sturin, yielded, on hydrolysis with acids, all the three "hexon" bases, sturin yielding as well amidovalerianic acid. The other protamines, such as clupein, scombrin, salamin, yielded only arginin, amidovalerianic acid, and an unknown residue. Cycloytelin contained besides these an aromatic group. Thus it appeared that the biuret color test is not peculiar to one certain "protamine group," and from this standpoint there is no reason to believe that all the proteids are derivatives of one protamine.

The analysis of animal proteids by Larrow and of plant proteids by Schulze, Mendel, and Levene, which have been made up to the present time, have revealed in all of them the presence of the three hexon bases. This would seem to corroborate the view that in proteids the biuret reaction is due to a "protamine." An objection to the latter assumption, however, can be found in the researches of H. Schiff.

H. Schiff has demonstrated that the biuret reaction can be obtained from different substances which contain two  $\text{CONH}_2$

groups combined together, either directly, like oxamide  $\begin{array}{c} \text{CONH}_2 \\ | \\ \text{CONH}_2 \end{array}$  or joined on a single carbon or nitrogen, like biuret  $\text{NH} \begin{array}{l} \nearrow \text{CONH}_2 \\ \searrow \text{CONH}_2 \end{array}$

or malonamine,  $\text{CH}_2 \begin{array}{l} \nearrow \text{CONH}_2 \\ \searrow \text{CONH}_2 \end{array}$ . Another requisite is that the  $\text{CONH}_2$  groups be combined in an open chain.

Thus H. Schiff has established the fact that the property giving the biuret color test is peculiar to more than one substance, that this property is due to the presence in the molecule, not of amido groups or amido acids, but of two of the radical  $\text{CONH}_2$  grouped in a certain way; that it is not very probable that a combination of "hexon" bases (which, according to Kossel's first surmise, constituted the protamine molecule) will necessarily give the biuret test; that, finally, in the protamines as well as in other proteids the peculiar color formed on addition of alkaline copper solution is due to the presence in their

respective molecules of a substance common to all of them, possibly, but perhaps not yet discovered. Attempts were also made to estimate the quantities of the different nitrogenous compounds in the molecules of different proteids, so as to establish a basis for their chemical classification. Hansemann has analyzed with this in view a great number of proteids, finding that the proportion of these constituents varied greatly with the character of the proteid. Henderson has, however, demonstrated that the temperature and the duration of the decomposition has a great influence on the formation of the different nitrogenous constituents, and thereby the conclusions of Hansemann lose much of their weight.

### III. SULPHUR.

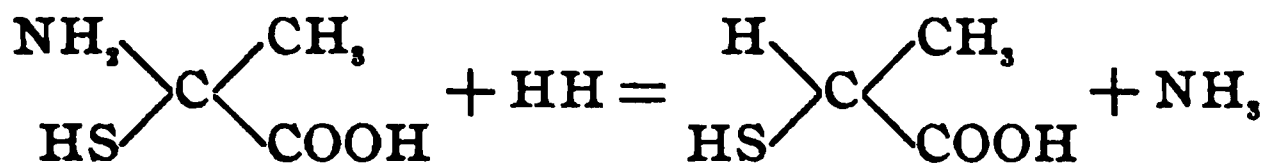
It has been accepted that the proteid molecule contains more than one atom of sulphur, and that the different atoms are in different forms of combination. This view is based on the fact that proteids heated with a solution of sodium hydroxide generally gave up part of their sulphur in the form of hydrogen sulphide, and the rest of the sulphur was detected only by means of strong oxidation, like fusion with sodium hydroxide and nitrate. Attempts have been made to establish the ratio between the different atoms. However, the methods employed by the older authors were not faultless, as the possibility of an oxidation of a part of the hydrogen sulphide into sulphuric acid (on heating with sodium hydroxide) was not excluded. The question thus needed new consideration, and such was given to it by F. N. Schultz. Great care was taken by the latter to prevent the possibility of oxidation of hydrogen sulphide, and in most experiments only about one-third of the total sulphur could be obtained in the form of hydrogen sulphide.

Very little has been known in regard to the nature of that part of the sulphur which could not be obtained as hydrogen sulphide. The opinion that it is in an oxidized state has been proved to be erroneous.

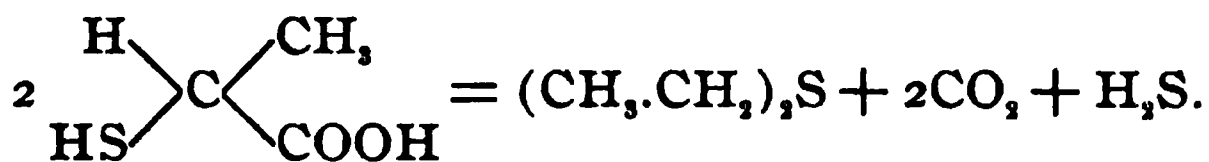
In recent years a few researches have appeared which throw some light on the subject, although none of them gives a final solution to the problem. Drechsel found among the basic decomposition products of the proteids, a substance which, on treatment with alkalis, yielded ethyl sulphide. He, therefore, concluded that the substance must be a sulphin base or a thetin compound; and that a quadrivalent sulphur was present in the proteid molecule.

A short time after Drechsel's discovery, Suter working in Baumann's laboratory, isolated from the decomposition products of proteids thiolactic acid, and very recently Morner has suc-

ceeded in obtaining, under the same conditions, cystein, which is a derivative of the former, as can be easily seen from the formulas.



Baumann has demonstrated further that similarly to the thetin compounds, the cystein or thiolactic acid yields ethyl sulphide on treatment with alkalies, according to the following formula :



Thus, another explanation was offered for the appearance of ethyl sulphide among the decomposition products of proteids. It must be remembered that both the substances ethyl sulphide and cystein (cystin) had been detected in animal secretions long before they could be obtained directly from proteids. The former was first identified in the urine of a dog by J. Abel; the latter by Baumann.

#### HALOGEN PROTEIDS.

Considerable study has been devoted to the halogen derivatives of the proteids; it was expected that the latter compounds would be of great aid in explanation of the constitution of the proteid molecule. The expectations, however, have not been realized up to the present date; although the future may be more successful.

#### SYNTHESIS.

Notwithstanding that little regarding the chemical constitution of the proteid molecule is established, attempts have already been made to obtain a proteid synthetically. In recent years the attempt was made by Lilienfeld, who stated in 1894 that he was successful in obtaining a synthetical proteid in the following way :

Curtius and Goebel found that if glycocoll-ethyl ester was allowed to stand, it yielded glycocoll and a biuret-giving substance which Lilienfeld claimed could form a condensation product with the ethyl ester of leucin, tyrosin, or aspartic acid, which product resembled peptone very closely.

More recently, Lilienfeld has modified his method and obtained proteids on condensation of phenol with glycocoll or with asparagin, etc.

Klimmer, however, justly remarks that Lilienfeld's substance could scarcely be considered a peptone on the following grounds :



1. The substance obtained by Lilienfeld yields readily, on decomposition, phenol and glyocol which other proteids do not, and the color which the substance takes, on treatment with alkaline copper solution, is not a color resembling the biuret reaction very closely.

Thus, little progress has been made towards the elucidation of the chemistry of the proteid molecule and its various parts. Attempts have been made to determine the weight of the molecule as a whole. According to Sabanejeff and Alexandrow, it is 14,900.

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P. A. LEVENE.



## THE PRESENT CONDITION OF THE COAL-TAR INDUSTRY.<sup>1</sup>

As the end of the century approaches it is interesting and instructive to look back and note the wonderful growth of the chemical industries and the great changes they have undergone, especially in the last few years, in which many of them have been revolutionized.

It may be of interest to some to consider the growth and present condition of one of the greatest of these, that of coal tar and its products.

This industry which originated in the endeavor to utilize a troublesome by-product, has grown to be the one which without doubt employs more scientific men in its study and development than any other, and a description of all its products and their manufacture would be a review of the greater part of the organic chemistry of to-day.

About 1822 coal tar was first distilled in England, but it was not until 1856, the date of the discovery of the first aniline colors, that the industry became an important one; and it is in the last twenty years only that it has attained its present gigantic proportions.

At first the entire supply of tar was derived from the distillation of coal in the manufacture of illuminating gas, but under the constantly increasing demand, new sources have been developed, and these latter may in time become our main supply.

The coal tar produced in modern gas plants is quite different from that of some years ago. Cast-iron retorts were then used and the temperature of carbonization was comparatively low. The tar in consequence was generally quite fluid and contained considerable toluene, xylene, and phenols, some naphthalene and free carbon. With the introduction of fire-clay retorts, a marked change was noted and to-day the extreme high heat produced by the use of regenerators yields a tar which, considered from the standpoint of the distiller, is of much poorer quality.

The aim of the gas manufacturer is to get the largest amount of gas of good quality that can be obtained from the kind of coal carbonized. The high temperatures employed to do this cause the volatile products as they are evolved during the distillation to be decomposed in contact with the intensely heated sides of the retort with separation of free carbon, and, as exhausters are universally used, this is drawn out with the gases and deposited with the tar.

<sup>1</sup> Chairman's address at the annual meeting of the Philadelphia Section, May 17, 1900.

The higher phenols and hydrocarbons are split up with formation of large quantities of naphthalene; therefore, the tar is heavier in gravity and thicker in consistency on account of the presence of more naphthalene and carbon and less of the liquid portions.

As the use of coal-tar products became more general, the demand for tar increased and in consequence the price advanced. The supply being to a certain extent fixed, manufacturers were stimulated to look for other sources of supply. Several plants were built in Europe and one in America having the production of tar and ammonia as their chief aim, but these were soon found to be unprofitable. Attention, however, had been called at an early date to the waste of these by-products in the manufacture of coke, and inventors without number entered the field with ovens designed to produce a good coke and at the same time save the tar and ammonia. A number of these, varying in minor details of construction, have been found to work well in practice,—besides, many beehive ovens have been provided with condensing plants for collecting the by-products. The tar obtained from these latter ovens and also from the gases of blast-furnaces is, however, quite different in composition from that obtained from gas works or improved coke ovens.

The temperature at which the coal is carbonized in the former being much lower, the tar contains practically no aromatic bodies, and when distilled yields oils which are free from naphthalene, benzene, and phenol, but instead contain compounds of the paraffin series, large amounts of higher complex phenols and paraffin; such tars are, therefore, of no value to the manufacturer of refined coal-tar products.

In the United States, owing to the extended use of oil and carburetted water-gas, the output of coal tar has been very much less in proportion to the population than in Europe, and it has been heretofore necessary to make up the deficiency by importing creosote oil and pitch. In the last few years, however, there has been a considerable addition to the domestic supply. A number of beehive ovens have been fitted with condensing plants and large batteries of improved coke ovens have been erected, and from these a fine grade of coke and considerable tar is obtained. The American coals appear to be much richer than those carbonized abroad.

In these ovens none of the charge is burnt to supply the heat necessary for the carbonization, as is the case with the older forms of ovens, and therefore, the yield of coke is very much larger, and may even amount to more than the analysis of the coal would seem to warrant, this being due to the deposition of carbon on the surface of the coke by the decomposition of a part of the tar as it is distilled.

The fact of a larger yield and purer quality of coke must, it seems, finally force other manufacturers to adopt improved ovens, and if even a part of the 20,000,000 tons of coke yearly produced in this country was made in such ovens with recovery of tar, we would pass from the condition of a shortage of supply to a veritable flood of tar, for even a small portion of which there would not appear to be a market.

One of the forms of ovens successfully introduced is the Semet-Solvay, of which about 300 are in operation in this country. Those interested in the subject will find a full description of them in an article by J. D. Pennock, which appeared in this Journal<sup>1</sup> in 1899.

The Otto-Hofmann ovens are used very extensively abroad, and through the kindness of Dr. Schniewind, chemist of the company, I am informed that 680 ovens are in operation in the United States, and that 400 are now being erected in Canada. The most interesting of these plants is that at Everett, near Boston, Mass., where 400 ovens are in successful operation. These have been fully described and illustrated by Dr. Schniewind in articles which have appeared in the *Progressive Age*. The plant is so situated that coal from Nova Scotia can be discharged directly from the steamers, and labor is reduced to a minimum by the use of every modern appliance for handling the materials used and produced.

The gas as it distils being higher in candle-power in the first hours of carbonization, this portion is collected by itself and after removal of tar and ammonia, is supplied to the city of Boston and vicinity. The gas coming off in the latter part of the distillation is used, after the tar has been removed, to heat the ovens. The coke is equal in quality to the best metallurgical coke and is sold for this purpose or broken into various sizes for domestic use.

It would seem that this novel and interesting application of the coke oven is destined to come into general use for large cities.

The tar from these ovens resembles the average retort tar except that it does not contain as much low-boiling hydrocarbons or phenol.

A certain amount of tar is also obtained from the manufacture of oil- and water-gas but they are of much less value than pure coal tar. The water-gas tar is especially difficult to utilize as it contains from 50 to 75 per cent. of water in the state of an emulsion which will not separate on standing.

In the United States tar is usually distilled into light oil, heavy oil, and pitch. The light oil comprises the first portions of the distillate until the oil, as it runs off, sinks in water. The

<sup>1</sup> This Journal, 21, 678.

entire distillate when mixed has a gravity from 0.93 to 0.98. Its nature has varied with the change in the tar as noted above, formerly they were quite fluid, but now in most cases they are semisolid from naphthalene.

The pitch remaining in the still after the distillation is known as soft pitch, and is adapted for roofing or paving purposes.

Formerly it was customary to run to hard pitch which was sent abroad to be used in the manufacture of compressed fuel; the anthracene oil obtained by this distillation was filtered and the anthracene pressed in hydraulic presses, making 40 per cent. anthracene. This was shipped to England and used in the manufacture of alizarin. At that time anthracene was one of the most valuable of the crude tar products, but the price has now fallen so low that it does not pay to export it, and there is very little sale for hard pitch as the manufacture of briquettes for fuel is carried on in a limited way only. The manufacture of anthracene has, therefore, been abandoned for some years.

The demand for creosote oil has, on the contrary, been constantly increasing owing to its extensive use in creosoting lumber, a number of plants for this purpose being in operation here.

Oil for this purpose is required to conform to certain specifications; formerly it was deemed necessary to have a large amount of tar acids, but now it is recognized that the naphthalene is a much more important agent in the preservation of lumber; and in consequence, specifications require 40 to 50 per cent. to be present, and in cold weather the oils are often entirely solid from separated naphthalene. In this connection, it is well to call attention to the fact that many specifications call for 50 per cent. of naphthalene and yet require the oil to be limpid at 90° F., which is an impossibility when such a large amount of naphthalene is present.

When we come to consider the refined products of coal-tar we can, in the short time at our disposal, mention only the most important. In general it may be said that each year greater purity is demanded by consumers, and a large number of the commercial products are practically chemically pure.

This branch of the industry has not made as great strides in the United States as it should. A severe blow was dealt when nearly all the protective duties were removed a few years ago. Formerly there was on the most of them a duty of 20 per cent. which enabled the American manufacturer to compete notwithstanding the higher wages ruling here.

The use of special labor-saving machinery which has done so much to enable our manufacturers to enter the markets of the world is not an important factor in this industry, which, owing to its nature, does not permit the extensive use of such labor-

saving devices, and where machinery can be used, we find the German manufacturers, who are our chief competitors, have the most improved devices in this line.

If we compare the estimates of cost of manufacture by American and German experts, the item of labor is seen to be a very serious one. For ordinary labor we must pay from 14 to 15 cents per hour, German estimates are based on 6 to 7 cents. In the pay of skilled mechanics the difference is even more striking: carpenters, masons, machinists, boiler and tank makers, receive from 30 to 45 cents per hour, while the prices abroad are scarcely 50 per cent. of these. This has a twofold effect on the industry: first, in increasing the item of repairs and maintenance, which, owing to the nature of the business, is a very large one, necessitating the constant renewal of parts destroyed in the processes. Second, it handicaps the manufacturer by requiring a larger outlay of capital to erect the plant than is the case abroad. A conservative estimate would be that an average plant would cost twice as much here as in Germany.

Of all the refined products, benzene has probably been subject to the greatest fluctuations. The demand for this article increased so rapidly that the price became very high, and efforts were made in all directions to perfect processes which would produce it independently of the gas works. It was at this time that the endeavor was made both in Europe and America to distil coal in retorts at the mines with the making of benzene as their prime object; but, as already stated, these were soon abandoned. A plant was also built in Ohio to manufacture benzene and its homologues from petroleum residues but without success.

Attention had been called at an early day to the large amount of benzene present in the coal gas, amounting to about twenty times as much as is present in the tar from the same gas. It was manifestly impossible to remove it from the gas without destroying, to a large extent, its illuminating power, but this objection did not hold good with the gas obtained from the improved coke ovens, and appliances were added to these plants to remove this benzene. A large number of such plants are in operation abroad at this time; the gas from the ovens after removal of tar and ammonia is forced through specially designed towers, in which the gas is brought into intimate contact with a fraction of oil from coal tar. This oil absorbs the benzene, and when saturated, is heated, and the crude benzene driven out. The product thus obtained is equal to about 90 per cent. benzene; that is to say, consists of about 70 per cent. benzene, 20 to 25 per cent. of toluene, and the balance of higher bodies. The introduction of these benzene extracting plants may be said to have been *too* successful, as the price has fallen to such an

extent that the extraction at present is hardly remunerative. We are, however, assured of a source of supply which can be readily increased as the demand warrants. The present supply is undoubtedly more than the demand; toluene, however, is not obtained in such large quantities by this method and as the demand is steadily increasing owing to many new uses, among them the manufacture of artificial indigo, the price has advanced so that it is now selling abroad at a higher price than benzene, while formerly the reverse was the case. At the present time there is no plant in operation in this country extracting the benzene from gas.

The low price of benzene permits it to be used in many industries as a solvent for the extraction of chemicals and drugs, and immense quantities are used abroad for enriching gas.

Naphthalene is one of the coal-tar products which is now manufactured on a very large scale in a great degree of purity. This article has advanced considerably in price owing both to the great demand, and to the fact that crude naphthalene is now readily sold without removal from the creosote oil for reasons stated above. Before the duties were removed, there were three factories manufacturing the article in this country; since it has been placed on the free list only one of these survives. The output is chiefly used as a substitute for camphor for destroying moths.

Crystal carbolic acid or phenol is one of the few tar products which has not suffered the general decline.

In all the varied new sources of supply of other tar products, none has been found which promises increased output of phenol. The coke oven tar does not appear to yield much phenol, so that while the supply is constant or perhaps increasing slightly, it does not keep pace with the large demand, the chief of which is for the manufacture of picric and salicylic acids. A limited amount of phenol is made in this country, and considerable refined from imported materials, but the great bulk comes to us in a finished condition from Europe.

Nitrobenzene, nitrotoluene, and other nitro compounds are made in one factory, the output being mainly used by manufacturers of colors and explosives. A certain quantity of rectified nitrobenzene, known as oil of myrbane, is used by manufacturers of soaps and oils.

Aniline oil which is made in such large quantities abroad is not made at present in this country. Its manufacture was undertaken a number of years ago by makers of colors but abandoned as it was found the article could be imported at less cost. A factory, however, is now being equipped for its manufacture, and in a few weeks will be in operation.

Acetanilide is made by two or three factories and they supply nearly all the requirements of this market.

When the tariff on coal-tar products was revised and most articles placed on the free list, for some reason, salicylic and benzoic acids were singled out from all other compounds and favored with the specific duty of 10 cents per pound. In consequence, a number of works are now producing the former acid, using imported phenol.

The finer organic compounds are apparently not produced except vanillin, which is being made by at least two if not three firms.

Notwithstanding the great competition of Europe in aniline colors, the American manufacturers have in the last few years made decided strides, although as yet they appear to have confined themselves to the older standard colors. They are aided by a duty of 20 per cent. with practically all their raw materials free. They still labor, however, under the disadvantage of having to import a great deal of their supplies. There are at present five factories in operation.

It will be seen from this rapid review that there is still a wide field for the chemist and manufacturer in this country; and with a gradual increase in the output of crude materials, it is to be hoped and expected that in a few years we will produce a large amount of the enormous quantity of these products now imported.

England appears to have fallen out of the race in the competition for the American trade, especially in the finer coal-tar products, and Germany is now in the lead, even competing with England in the cruder preparations. To show the important position held by Germany, attention is called to the statistics compiled by the German government up to July 1898, on which date there were 25 factories devoted to anilin and anilin dyes, and 48 establishments which made dyestuffs, carbolic acid, and other coal-tar preparations. Among the exports for 1898 were:

9,321 metric tons, alizarin,

19,712 metric tons, coal-tar colors.

12,360 metric tons, aniline oil and salts.

In this latter class the exports of 1898 were nineteen times as much as in 1883.

H. W. JAYNE.



## NOTE.

*Qualitative Tests for Boracic Acid.*—It seems not to have occurred to authorities on the subject to test the effect of the alcoholic vapors of boracic acid on turmeric paper. We find that, if the test is applied in the following manner, the presence of boracic acid in minerals is rendered more certain and delicate.

Use a test-tube about 2.5 cm. in diameter and 20 cm. long. Put into the tube about 0.1 gram of the substance, 0.5 cc. hydrochloric acid, and 10 cc. wood alcohol. Boil vigorously down to small bulk, agitating the lower end of the tube in flame of burner, and holding the moistened end of a piece of turmeric paper just outside the mouth, so as to catch the vapors. Boracic acid will finally color the turmeric a characteristic red. Now, if the turmeric is placed vertically on the side of a beaker so as to dip into a little distilled water to which a few drops of ammonia have been added, a pinkish to deep purple or blue will be produced, in marked contrast to the red produced by the ammonia on the end of the paper unaffected by the vapors.

LOS ANGELES, CAL.,  
July 2, 1900.

E. M. WADE AND M. L. WADE.

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## NEW BOOKS.

THE CALCULATIONS OF ANALYTICAL CHEMISTRY. BY EDMUND H. MILLER, Ph.D. New York: The Macmillan Co. 1900. viii + 183 pp.

In nearly all of the books published on the calculations of analytical chemistry there is a distinct statement in the preface that the book has been published with the idea of preparing the student to pass certain examinations. This pernicious system, fortunately, has not invaded the American text-book to anything like the same extent as it has the English books of the same class. There has been in the past scarcely any attempt to lay down general principles in regard to chemical calculations. This book is a decided advance in an attempt to treat the subject from a broad point of view. Just how far it will succeed remains to be seen, for there are hardly any two teachers who will treat the subject in the same way. All will, I believe, agree that it is a distinct advance to present such a subject entirely free from formulas. The student is asked to solve the problems, applying his general knowledge of chemistry. If he has been successful



in applying and understanding the laws, he can then construct his formulas if he so wishes.

The book consists of ten chapters divided as follows: calculations of chemical equivalents and atomic weights; formulae and percentage; mixtures having a common constituent; equations; use of factors; volumetric analysis; density of solids and liquids; gases; calorific power; electric and electrolytic calculations for direct currents. In addition there is a series of tables of weights, measures, specific gravities, factors, logarithms, etc., which will be found useful to any one having occasion to make any calculations. There will, probably, be a greater difference of opinion over the chapter on normal solutions than over any other. The author's development of the subject is satisfactory, but he has not exhausted the possibilities for clear treatment of a subject which can be made particularly attractive and instructive. The book, if used in connection with classroom work, will undoubtedly be of great value, and should help the student to a much clearer understanding of the quantitative values of chemical laws.

HENRY FAY.

COLOUR: A HANDBOOK OF THE THEORY OF COLOUR. BY GEORGE H. HURST. New York: D. Van Nostrand Co. 1900. Price, \$2.50.

The author of this book of 158 pages is a member of the Society of Chemical Industry, and is already known by his works on soaps, lubricating oils, painters' colors, and a "Dictionary of Coal Tar Colours." In this handsomely printed volume he endeavors to present to those familiar with the practical printing and dyeing of textile fabrics, and the mixing of colors for artistic effects, the theory of color, its cause and production, together with some account of the instruments used by scientific men in the study and measurement of color. The opening chapter treats of the prismatic colors, the spectroscope, wave motion, phosphorescence, fluorescence, luminosity, and so forth, in the compass of 31 pages. Other chapters deal with the theories of color as propounded by Young, Helmholtz, Brewster, and Maxwell, with the physiology of light, with contrast, and with the application of color to decoration and design. In his preface Mr. Hurst acknowledges his indebtedness to the manuals of Chevreul, Benson, Rood, and Church.

The book is illustrated freely, containing no less than 72 cuts and 10 full-page colored plates; unfortunately for readers the plates, many of which contain several figures, are simply numbered and bear no references to the pages on which the text occurs that explains the figures, or that the figures illustrate. The figures on plate IV refer to texts on pages 79, 105, 106, and 114, and yet the plate faces page 48, and no indication is given of these references. It is true that the plates should be regarded as illustrating the text, but if the latter is first examined it will be found that references are not much clearer; on page 63 a reference to "Fig. 2, Plate 3" should read "Plate II., Fig. 2," and that to "Fig. 3" of the same plate should read "Fig. 4." Throughout the book, the plates bearing Roman numerals are referred to by Arabic figures, and lack of uniformity in the sequence of "Plate" and "Fig." increases the confusion. This unhappy blemish prevents easy study of the brilliant plates, but can be corrected in a second edition. There is an index and the volume is well bound. H. CARRINGTON BOLTON.

A POCKET BOOK FOR CHEMISTS. BY THOMAS BAYLEY. New York: Spon & Chamberlain; London: E. & F. N. Spon, Ltd. Seventh edition. 'xii + 559 pp. Price, \$2.00.

This book is already well known to chemists. The new edition, according to the preface, has been "rearranged and to a large extent rewritten." In spite of this much is yet to be desired in the arrangement of the tables and many of them might be presented in a much simpler and more compact form. In the selection of matter, it seems to the reviewer, that the author has attempted to cover too much ground and that many of the tables are so seldom used and are so readily accessible to any one having occasion to use them that they could well be cut out, while others such as those under the sections X, alcohol, XI, beer, and XII, sugar, might well be left for the special pocket-books gotten out for these industries. Of course there is no objection to the insertion of these tables except that they add to the size of the book and make the useful tables less readily turned to. In spite of these defects the book contains much valuable information and many tables in every-day use by chemists.

RICHARD K. MEADE.

**FIELD TESTING FOR GOLD AND SILVER.** A Practical Manual for Prospectors and Miners. BY W. HAMILTON MERRITT. London: Crosby & Lockwood; New York: D. Van Nostrand Co. 16mo. x + 144 pp. Illustrated. Price, \$1.50.

This is a book for the prospector and contains full directions for such rough tests as can readily be used in the field. Part I (72 pp.) is devoted to assaying, Part II to practical mineralogy and geology, and Part III contains a glossary of useful mining terms and a list of common rock-forming minerals and rocks. The booklet is bound in flexible leather, and is of a size suitable for pocket use.

E. H.

**THE MANUFACTURE OF VARNISHES: OIL CRUSHING, REFINING AND BOILING.** From the French of Ach. Livache, extended and adapted to English practice by John Geddes McIntosh. London: Scott, Greenwood & Co. 1899.

This book contains some information about raw materials which may interest the novice, nearly half the space being devoted to this, the greater part of which is reasonably correct. The author has collected a good deal of somewhat antiquated chemical literature on resins, the value of which is well indicated by the luminous observation on p. 18 that "The data are of no value, except in regard to the variety of copal which is referred to; and this is exactly the point which the investigators have almost invariably omitted to supply;" and "of little or no value to the practical varnish maker." The book is equally remarkable for what it contains and what it leaves out. For example, no reference is made to the almost universal practice of hardening rosin with lime; and it would be hard to compress more ignorance of the facts and of modern literature on asphaltums into a sentence than the following: "In its composition this mineral (Manjak) is similar to the pitch of Trinidad, to the gilsonite of Utah and the Canadian albertite." Nothing is said about oil-soluble aniline colors, but the incorrect statement is made that indigo-carmin is soluble in oil (p. 86). The present reviewer is not competent to criticize the chapter on spirit varnishes, except on one or two points. Shellac varnish is said to be made by dissolving one part of shellac in 5 to 12 parts of alcohol; such a solution can not be sold in this country, and probably not in England; regular shellac varnish is made with

5 pounds of shellac to  $6\frac{1}{2}$  pounds of alcohol. Much is said about wax in shellac but none of the practical modern methods of removing it are given. A brief and valueless section is given to the 'important subject of asphaltum varnishes. The preparation of raw linseed oil is well described; but a lot of venerable and worthless recipes for bleaching it are given, reference being sometimes made to "water-white" or "colorless" oil, something never yet produced, even approximately. The author seems ignorant of modern methods of oil-treatment, the most recent one referred to being Hartley's, which had been known and abandoned in this country before Hartley patented it.

Aside from references to Mulder and Chevreul (not very new) the treatment of the subject of driers is unsatisfactory. The fact is that the essential thing is to get a certain amount of lead or manganese into the oil, it makes no difference whether we use oxides, borates, or anything else; the other factor is the temperature needed. Zinc and magnesia salts are of no value, and are long out of date. Contrary to the statement on pp. 263-4, this reviewer has made excellent driers of nickel and cobalt, but they are too costly.

The section on oil and resin varnishes is especially unsatisfactory. It seems as if the translator ought to have been able to get some valuable matter for this, since the English varnish-makers produce varnishes which are up to date and of great excellence; but such does not appear to have been the case. The curious statement is several times made that in melting resins it is better to work with small quantities, 3 to 5 pounds, because the discoloration, produced by contact with the metal of the melting-pot, is less. Both theory and practice ought to show that the larger the vessel and the amount of resin the smaller is the heating surface per pound of resin, and the less the discoloration. It is, therefore, possible to melt 125 pounds at a time, which is the common American practice, and make a paler product than can be made in the laboratory. Before the use of the thermometer in this work the varnish-maker had various tests of heat, such as dropping in a bit of onion peel, which would brown and shrivel, or a feather, which would curl up with the heat when the temperature had reached a certain

point; but this fried-onion and burnt-feather business has now gone out of practice, notwithstanding what is said about it in this treatise.

One of the chief authorities quoted is Violette. Now Violette worked about half a century ago, and if he ever knew anything about practical varnish-making, which is doubtful, his book is out of date; and this is the general verdict to be passed on this book. It is misleading to the student, and of no value to the varnish-maker.

A. H. SABIN.

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### BOOKS RECEIVED.

**The Manufacture of Varnishes.** Oil crushing, refining, and boiling, and kindred industries; describing the manufacture and chemical and physical properties of spirit varnishes and oil varnishes; raw materials; resin; solvents and colouring principles; drying oils, their extraction, properties, and applications; oil refining and boiling; the manufacture, employment, and testing of various varnishes. Translated from the French of Ach Livache, Ingenieur civil des mines. Greatly extended and adapted to English practice with numerous original recipes by John Geddes McIntosh. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1899. vii + 403 pp. Price, \$5.00.

**Commercial Fertilizers.** By J. H. Stewart and B. H. Hite.—Bulletins Nos. 63 and 65. **Sugar Beet Investigations in 1899.** By J. H. Stewart and B. H. Hite.—Bulletin No 64. West Virginia Agricultural Experiment Station, Morgantown, W. Va. 82 pp.

**Field Testing for Gold and Silver.** A Practical Manual for Prospectors and Miners. By W. Hamilton Merritt. London: Crosby & Lockwood. New York: D. Van Nostrand Co. 16 mo. x + 144 pp. Illustrated. Price, \$1.50.

**Charbon (Anthrax).** Further investigations and suggestions, with summary and conclusions. Second series No. 60, Bulletin of the Agricultural Experiment Station of the Louisiana State University and A. & M. College, Baton Rouge, La. 28 pp.

Bulletin No. 57.—**The Smuts of Illinois' Agricultural Plants.** 72 pp. Bulletin No. 58.—**Composition and Digestibility of Corn-fodder and Corn Stover.** 10 pp. Bulletin No. 59.—**Orchard Management.** University of Illinois Agricultural Experiment Station, Urbana, Ill. 26 pp.

**Gardening under Glass.** Bulletin No. 170. The North Carolina College of Agriculture and Mechanic Arts, Agricultural Experiment Station, West Raleigh, N. C. 24 pp.

**Proceedings of the Twenty-fourth Annual Meeting of the Pharmaceutical Association of the State of South Carolina, held in Charleston, S. C., May 17, 1900.** 30. pp.

The Chemistry of the Metals. By J. H. Kastle, Lexington. 1900. vi + 198 pp. 8vo.

Annali del Laboratorio Chimico centrale delle Gabelle. Diretti dal Dr. Vittorio Villavecchia. Volume IV. Roma: Tipografia Elzeviriana di adelaide ved. Pateras. 1900. 528 pp.

The Apple Orchard.—Bulletin No. 49. Agricultural Experiment Station of the University of Missouri, Columbia, Mo. January, 1900. 21 pp.

An Outline of the Theory of Thermodynamics. By Edgar Buckingham, Ph.D. (Leipzig). New York: The Macmillan Co. 1900. xi + 205 pp. Price, \$1.90.

L'Eau dans l'Industrie. Par H de la Coux. Paris: Vve Ch. Dudon, Éditeur. 1900. 496 pp. Price, 15 francs.

Inspection and Analysis of Foods.—Bulletin No. 86. 51 pp. Kentucky Forage Plants; analyses of Some Kentucky Grasses.—Bulletin No. 87. 68 pp. with 14 plates. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky.

Essentials of Medical and Clinical Chemistry, with Laboratory Exercises. By Samuel E. Woody, A.M., M.D. Fourth edition, revised and enlarged. Philadelphia: P. Blakiston's Son & Co. 1900. viii + 243 pp.

An Ephemeris of Materia Medica, Pharmacy, Therapeutics, and Collateral Information. July, 1900. On Acetic Acid as a Substitute for Alcohol in Extracting the Active Principles of Some Official Drugs. By Edward R. Squibb, M.D. 10 pp.

Corn Culture in North Carolina.—Bulletin No. 171. The North Carolina College of Agriculture and Mechanic Arts, West Raleigh, N. C. May, 1900. 20 pp.

Twenty-third Annual Report of the Connecticut Agricultural Experiment Station for 1899. Part III.—Papers on availability of Nitrogen, fertilizers for forcing-houses, insect notes, on tobacco diseases and remedies, fertilization of melons, notes on Fungi, tobacco experiments, and vegetable proteids. New Haven, Conn. 1900. viii + 195 pp.

(1) H. R. 11350. A BILL to establish the National Standardizing Bureau. (2) Document No. 625, Letter from the Secretary of the Treasury, transmitting, with accompanying communications, a draft of a bill for the establishment of a National Standardizing Bureau. (3) Hearing before the committee on coinage, weights, and measures, House of Representatives, May 3, 1900. Superintendent of Document Room, House of Representatives, Washington, D. C.

# THE JOURNAL

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### THE RELATIVE VALUES OF THE MITSCHERLICH AND HYDROFLUORIC ACID METHODS FOR THE DETER- MINATION OF FERROUS IRON.<sup>1</sup>

BY W. F. HILLEBRAND AND H. N. STOKES.

Received July 27, 1900.

**A**MONG determinations in mineral and rock analysis, upon the accuracy of which great stress is laid, is that of iron in the ferrous condition. It is of special importance because an error attaching to it affects in like degree but opposite direction the ferric iron that is also nearly always present. Up to about the year 1867, the only method for its determination giving at all satisfactory results was that of A. Mitscherlich,<sup>2</sup> depending on the decomposition of the mineral at high temperature by rather strong sulphuric acid (3 parts acid to 1 part water by weight) in a sealed tube from which air has been expelled, and subsequent titration of the ferrous iron by permanganate. When pure hydrofluoric acid became a commercial article, the above method gave place in large measure to one depending on the decomposition of the silicate by a mixture of dilute sulphuric and hydrofluoric acids at atmospheric pressure and a tempera-

<sup>1</sup> Published by permission of the Director of the United States Geological Survey.

<sup>2</sup> *J. prakt. Chem.*, 81, 116 (1860).

ture not above  $100^{\circ}$  C., care being taken as before to prevent contact with air.<sup>1</sup>

It became known in the laboratory of the United States Geological Survey fully twelve years ago that the two methods generally give discordant results when applied to the same rocks, the Mitscherlich method in such cases always showing the higher figure for ferrous iron. With low percentages of iron the discrepancies were not very great, but they seemed, in general, to increase as the ferrous oxide rose, until, with a rock showing 10 per cent. ferrous oxide by the hydrofluoric acid method, the Mitscherlich method might give 12 per cent. Experiments with artificial ferrous salts threw no light on the subject, for both methods gave with them the same sharp and concordant results.

Until very recently no cause suggested itself whereby the discordance could be explained. In theory, the Mitscherlich method seemed perfect, and it was concluded that, given entire decomposition of all ferruginous minerals, the determinations made by it were nearer the truth than those by the hydrofluoric acid method. That the reverse is true in most cases, appears as the result of work done in this laboratory in an entirely different connection.

In the first place, it had been found by long experience that nearly all rocks carry small amounts of sulphides—pyrite, pyrrhotite, or both—often visible to the eye, but more often in such small amount as to escape direct observation. One of us (Stokes), in an investigation now in progress on the oxidizing action of ferric salts on sulphur, pyrite, and other sulphides, has found that this action is vastly more rapid and complete than has hitherto been suspected; that not only is the metal of the sulphide oxidized, but the sulphur to sulphuric acid as well.

The application of these observations to rock analysis shows that the presence of 0.01 per cent. of sulphur in any unoxidized form may produce a maximum error of 0.135 per cent. in the ferrous oxide determination and the not infrequent amount of 0.10 per cent. of sulphur will multiply this error by 10. One atom of sulphur (32) requires for its complete conversion into trioxide the oxygen of three molecules of ferric oxide (480), which then becomes six molecules of ferrous oxide (432). The

<sup>1</sup> J. P. Cooke: *Am. J. Sci.* (2), 44, 347 (1867).



case is still worse with the sulphide, since not only the sulphur, but its accompanying metal must be oxidized. The above percentages of sulphur evolved as hydrogen sulphide and fully oxidized would involve errors in the ferrous oxide determination of 0.18 per cent. and 1.80 per cent., respectively. The error caused by sulphides tends to become greater the more there is present of either or both sulphide or ferric salt. Now the highly ferruginous rocks usually carry more ferric iron than the less ferruginous ones, and they are often relatively rich in pyrite and pyrrhotite; hence the increased discrepancy between the results by the two methods, as the iron contents of the rock rise, is fully in accord with the above explanation.

The following experiments made by Stokes (somewhat out of their contemplated order in his investigation referred to) bear out the above statements most fully and show that the Mitscherlich method for rocks and all minerals which contain even a trace of free sulphur or sulphides is no longer worthy of a moment's consideration.

*Experiment 1.*—0.0010 gram pyrite was heated with 25 cc. of a sulphuric solution (1 part acid to 3 parts water by weight) of ferric ammonium sulphate (0.0470 gram of ferric oxide) in a horizontally-lying sealed tube for six hours at 175° to 195° C. All air had been carefully replaced by carbon dioxide. The pyrite had nearly disappeared, and titration with permanganate showed a consumption of oxygen equivalent to 0.0068 gram ferrous oxide. Complete oxidation of the pyrite would have required oxygen equivalent to 0.0090 gram ferrous oxide.

*Experiment 2.*—This was exactly like the first, except that 0.0013 gram pyrite was used. Permanganate was reduced equivalent to 0.0090 gram ferrous oxide. Had oxidation been complete the figure would have been 0.0117 gram.

It is quite possible that in both of these experiments the oxidation would have been complete had the pyrite been disseminated throughout a greater space in the tube, as is the case when rocks and minerals are treated, because of the presence of a gram or thereabouts of diluting quartz and silicates.

Had precisely similar experiments been made with rock powders carrying 0.10 per cent., and 0.13 per cent., of pyrite with

4.7 per cent. of ferric oxide and no ferrous oxide, the following erroneous results might have appeared :

	I.	II.
Ferrous oxide.....	0.68	0.91
Ferric oxide.....	4.00	3.76

To overcome the possible objection that the foregoing experiments were not conclusive as to the worthlessness of the Mitscherlich method in presence of sulphides because the concentration of the acid was very different from the normal, the following sealed tube experiments were made with acid of the normal strength (3 parts acid to 1 part water by weight) without any ferric salt, the belief being that the stronger acid, under the conditions of the experiment, would itself act as an oxidizer.

*Experiment 3.*—Pyrite 0.0016 gram. Three hours at 195° C. Solution only partial. Consumption of permanganate equivalent to 0.00117 gram ferrous oxide.

*Experiment 4.*—Pyrite 0.0032 gram. Twelve hours at 220° C. Solution perfect. Odor of sulphur dioxide apparent on opening tube. Consumption of permanganate equivalent to 0.01742 gram ferrous oxide.

*Experiment 5.*—Sulphur 0.0021 gram. Three hours at 195° C., and, as the sulphur had not disappeared, further six hours at 250° C. Entire disappearance of the sulphur. Consumption of permanganate equivalent to 0.01320 gram ferrous oxide.

*Experiment 6.*—Sulphur 0.0039 gram. Twelve hours at 220° C. Entire disappearance of the sulphur and strong odor of sulphur dioxide on the opening tube. Consumption of permanganate equivalent to 0.03619 gram ferrous oxide.

In experiments 4, 5, and 6, where decomposition was complete the consumption of permanganate is considerably less than theory requires, but this is explained by the escape of not a little sulphur dioxide on opening the tube. Had a ferric salt been present the consumption of permanganate would undoubtedly have reached that required by theory.

It might be supposed from the foregoing that a similar error would affect ferrous iron determinations by the hydrofluoric acid method. However, experiment has shown that with the amounts of sulphide usually found in igneous rocks their effect is negligible, though by increasing the amount of sulphide the

effect becomes more and more apparent because of the greater surface of pyrite exposed to the action of the ferric iron of the rock.

Under the conditions of the Mitscherlich method, on the other hand,—a temperature of  $150^{\circ}$ – $200^{\circ}$  C., and even higher, high pressure, much longer time of action, and impossibility of escape of any hydrogen sulphide that may be formed,—the sulphur of the sulphides becomes nearly, if not quite, fully oxidized to sulphuric acid, at the expense of the ferric oxide in the rock, with the production of an equivalent amount of ferrous oxide in addition to that resulting from the iron of the sulphide itself.

In order to obtain quantitative data regarding the effect of pyrite on the ferrous iron estimation by the hydrofluoric acid method, the following tests were recently made by one of us.

Part of a fine crystal of pyrite was rather finely powdered and boiled out with dilute sulphuric acid, which extracted considerable ferrous iron, derived presumably from admixed or intergrown pyrrhotite, or from superficial oxidation of the powder, since a second boiling with fresh acid afforded a negative test for ferrous iron. After washing by decantation with water, followed by alcohol and ether, the powder was dried and further pulverized. A quarter of a gram of it, when treated with dilute sulphuric and hydrofluoric acids in a large crucible by the Cooke method for ferrous iron, then rapidly filtered through a very large perforated platinum cone fitted with filter-paper, required but two drops of a permanganate solution representing only 0.0032 gram ferrous oxide to the cubic centimeter.

That the error obtaining under the conditions prevailing in rock analysis might be ascertained, successive portions of one gram each of a hornblende schist free from sulphur and carrying 10.09 per cent. ferrous oxide as the mean of several determinations and 4 per cent. ferric oxide, were mixed in a 60 cc. platinum crucible with 0.02, 0.025, and 0.10 gram, respectively, of the above purified pyrite powder. This mixture was then treated with hydrofluoric and sulphuric acids as above, the water-bath being at boiling heat for one hour. The cooled contents of the crucible were poured into a platinum dish containing water and titrated rapidly nearly to an end. Then, in order to get rid of the pyrite, which would obscure the end-reaction by

its reducing effect upon the permanganate, the solution was filtered as above and in the clear filtrate the titration was carried to completion. The results were 10.02, 10.16, and 10.70 per cent. ferrous oxide. Inasmuch as the smallest of these three charges of pyrite was several times greater than what may be considered an unusually high amount for an igneous rock, it is very evident that for all practical purposes the influence of pyrite on the ferrous iron estimation by the Cooke method is negligible. At the same time, it is to be borne in mind that with increased content, either of ferric iron or of pyrite, an increased amount of pyrite will be attacked and that the extent of this attack is undoubtedly influenced by the degree of fineness of the pyrite powder.

All users of the method have noticed the rapid disappearance in hydrofluoric solutions, when titrating ferrous iron, of the pink color produced by an excess of permanganate. If much ferrous iron be present, many cubic centimeters of permanganate can be added without causing more than a transitory pink coloration. The solution takes on, however, in ever-increasing intensity, the red-brown color characteristic of manganic salts. It seems that manganous fluoride in acid solution is very susceptible to oxidation by permanganate, for the above-mentioned changes take place when permanganate is added to sulphuric and hydrofluoric acids containing some manganous sulphate.

WASHINGTON, July, 1900.

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## ON THE DIGESTION AND ASSIMILATION OF PENTOSES AND FURFUROIDS.

BY C. F. CROSS, E. J. BEVAN, AND J. S. REMINGTON.

Received July 16, 1900.

THE furfural-yielding constituents of plant tissues continue to be designated by the majority of observers as pentosans. It is probable, however, that the group of natural products thus constituted are of more varied characteristics.

It must be noted first that we have no specialized form of pentosane comparable with starch and that the substances described as such are products isolated by chemical processes in the laboratory and devoid of the well-marked individuality and properties of the hexose-anhydride. We are not aware of any

evidence upon which the individuality of the best known of the reputed pentosanes, *viz.*, "Holzgummi," has been finally established.<sup>1</sup> Generally this group of substances is investigated in terms of furfural, obtained by boiling with condensing acids; and the relation of this aldehyde to the pentoses is indirect and of course not exclusive. Several of the now well-known oxidized derivatives of the hexose-carbohydrates are similarly condensed to furfural; of these we can call to mind: (*a*) Glycuronic acid; (*b*) the osones or ketoaldoses obtained by Fischer from the osazones and more recently and directly by ourselves by the action of hydrogen peroxide on the hexoses;<sup>2</sup> (*c*) a number of imperfectly defined products of oxidation of the hexoses and their polyanhydrides obtained both by laboratory and natural processes.<sup>3</sup>

Lastly it must be noted that investigation has failed to identify the pentoses as such occurring in the plant and the conclusion generally accepted at this date with regard to their formation is that they are not direct products of the assimilation process but originate from hexoses by processes of oxidation or internal change.<sup>4</sup>

Complementary confirmation of the exceptional physiological relationships of the pentoses is also supplied by the facts (1) that they are entirely resistant to alcoholic fermentation (yeast) and (2) are not assimilated by animal digestion.

From this brief résumé of the present state of our knowledge we draw the following conclusions: (*a*) That the group of furfural-yielding constituents of plants may comprise in addition to petosans, oxy-hexoses (respectively anhydride) representing intermediate terms of a complex hexosan-pentosan series; and in view of this probability we prefer as a group designation the term furfuroid, and (*b*) that such oxyhexoses may yield to yeast fermentation and to animal assimilation.

Since these furfuroids are constituents of cellular tissues the question of alcoholic fermentation can only be studied by way of the products of acid hydrolysis. In so far as these products are pentoses they resist fermentation. This has been finally

<sup>1</sup> "Kohlenhydrate," II, p. 202, Tollens.

<sup>2</sup> *J. Chem. Soc.*, 73, 463 (1898); Morrell Crafts: *Ibid.*, 75, 786 (1899).

<sup>3</sup> *Ber. d. chem. Ges.*, 27, 1061: Krüger and Tollens: *Ztschr. angew. Chem.*, 1896, Heft 2.

<sup>4</sup> "Kohlenhydrate," II, p. 60.

established by the very careful investigation of Tollens;<sup>1</sup> at the same time we and other observers have studied cases of yeast fermentation in which there has been a considerable disappearance of the furfuroids from solutions in which they exist in a more or less fully hydrolyzed form.

In his investigation of this result Tollens arrives at the conclusion that the disappearance of the furfuroids is accompanied by the appearance of acid products; also that this effect is not inconsistent with the view that the products reacting in this way are pentoses.<sup>2</sup> Still the question is by no means finally elucidated and the incompleteness of the present solutions of the problem involved should be recognized.

In regard to the problem of animal digestion and assimilation we have to notice the results of investigation from two points of view. The pentoses proper have been investigated by Ebstein<sup>3</sup> who found that xylose is not assimilated, being voided in unchanged form in the urine and Salkowski<sup>4</sup> whose observations on arabinose led to the following conclusions: "Von dem jeden Thiere eingegebenen 10 g. Arabinose wurde etwa 1/5 unverändert durch den Harn ausgeschieden: das Blut enthält wenig, die Muskeln reichlich Arabinose. In der Leber fand sich gewöhnliches Glykogen und nicht, wie gehofft ein Pentosan. Die Resorption der Arabinose erfolgt schnell u. vollständig."<sup>5</sup>

On the other hand the furfuroids of fodder plants have been investigated by a number of observers who have variously estimated the proportion digested at from 40–90 per cent. These numbers represent for the most part the percentage ratio of the furfuroids disappearing in the digestive process, but they do not attempt to deal with the further question of assimilation. This more elaborate problem has recently been solved in a typical case by O. Kellner and A. Kohler.<sup>6</sup> Oxen were fed upon a rye straw which had been previously extracted by boiling with alkaline lye—the product containing:

78.6 per cent. Rohfaser with

31.1 per cent. Furfurol gebende substanz.

<sup>1</sup> Stone and Tollens: *Ann. Chem. (Liebig)*, 249, 257; Tollens: *J. Fed. Inst. Brewing*, 1898, 451.

<sup>2</sup> Tollens: *Ibid.*

<sup>3</sup> *Archiv. Pathol. Anat.*, 129, 401.

<sup>4</sup> *Central bl. Med. Wiss.*, 1893, No. 11.

<sup>5</sup> *Ber. d. chem. Ges.*, 1893, 896.

<sup>6</sup> *Landw. Vers. Stat.*, 1900, 53, 1, 474.

This product was added to the "Grundfutter" specially designed "zur Deckung des Mindestbedarfes des Thiers". The following results were obtained: Of the total product 95.8 per cent. was digested, and of the total available energy, 63.1 per cent. contributed to the formation of flesh and fat. The "furfuralgebende Substanz" contributed its proportion to the result and generally the cellulosic substance thus prepared has approximately the same feeding characteristics and value as starch.

But we find no records of investigations in which the furfuroids have been previously isolated by processes of acid hydrolysis. In absence of such results the proportions determined above are open to the objection that they are complicated by the unknown factor of digestive hydrolysis. To further elucidate the problem, therefore, we have carried out feeding experiments with the complex of products obtained from brewers' grains by digestion with dilute sulphuric acid (1 per cent.  $H_2SO_4$ ) in an autoclave at a temperature of  $130^\circ$ . Under these conditions the furfuroids are selectively attacked and constitute 80–90 per cent. of the total soluble extract. The products in this form we have previously investigated and have found to be fully hydrolyzed from the numbers for cupric reduction; *viz.*, 110–120 (dextrose = 100) and yields of osazones.<sup>1</sup>

The acid extract is neutralized ( $CaCO_3$ ), filtered and evaporated. On distillation with hydrochloric acid of 1.06 sp. gr., the extract yielded 39.5 per cent. furfural calculated to the total dry weight. To convert the product into a form in which it could be easily administered to the animal (rabbit) as a foodstuff, it was mixed with a strong solution of gelatin at  $20^\circ C$ . and then with sufficient bread to give, when cold, a solid granular product. With this artificial food was associated a due proportion of fresh vegetable food; *viz.*, carrot and cabbage. The experiments were conducted with the usual precautions, in parallel series, one animal receiving the diet as above, a second receiving this same diet less the artificial furfuroid constituent. The details of the experiment are published elsewhere and need not be reproduced here.<sup>2</sup>

<sup>1</sup> *J. Chem. Soc.*, 1897, 1001–1010.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1900, April 30.



The results obtained established the following high proportion (per cent.) of digestion and assimilation of the total furfuroids of the mixed diet

96.4      98.4      97.3      96.4      94.5

which are certainly minimum numbers for the special group of furfuroids under investigation. No pentoses or other furfural-yielding products were present in the urine, which was examined from time to time.

It may be concluded from these results that the typical furfuroids of cereal tissues when fully hydrolyzed are digested and assimilated by the herbivora as completely as starch and its products of hydrolysis. In this respect they differ from the pentoses and their anhydrides.

In view of these results and the exceptional physiological history of this group of constituents of plant tissues, which is by no means fully elucidated, we consider the term "furfuralgebende substance," or more shortly "furfuroid" is to be preferred as a general designation, reserving the term pentosan for its strict use; *i. e.*, as applied to a pentose-anhydride ( $\text{H.C}_5\text{H}_{10}\text{O}_5 - \text{MH}_2\text{O}$ ).

4 NEW COURT, LONDON, AND LANCASTER,  
ENGLAND, May 10, 1900.

## ESTIMATION OF PYRRHOTITE IN PYRITES ORE.

BY F. B. CARPENTER.

Received August 15, 1900.

SINCE the introduction of pyrites into the manufacture of sulphuric acid, industrial laboratories have been frequently called upon to make analyses of pyrites ores to determine their quality for manufacturing purposes. In order to determine the relative value of these ores it is not only necessary to determine their sulphur content, but it is also essential that an estimation be made of those sulphides, which are difficult to decompose in the furnace. Fairly satisfactory methods have been described for the determination of zinc, arsenic, copper, etc., but I have heretofore seen published no satisfactory methods for the estimation of pyrrhotite. It is well known by acid makers that it is difficult to get the sulphur from this material, especially in lump burners, and as it is contained in nearly all our domestic ores to



a greater or less extent, the importance of its presence should not be overlooked.

The usual method for the determination of pyrrhotite in pyrites is based on its magnetic properties, and briefly stated, is carried out as follows: About 25 grams of the material, ground to pass a 60-mesh sieve, is spread out on a piece of glazed paper, and a magnet of the horseshoe type is passed backward and forward through small portions at a time. As soon as the poles of the magnet are loaded with attracted material the bridge between them is broken down with the armature, so that as much of the mechanically retained pyrites as possible may be dislodged; then after striking the magnet several times sharply with the bare hand to further free the magnetic portion from the pyrites, the adhering substance is transferred to a clean sheet of paper; then another portion of the ore is treated like the first, cleansing and transferring the attracted part in the same way, and this continued until the whole amount has yielded all magnetic matter. The portion removed to the second paper is still far from pure, and the cleansing operation is repeated for a second and third time in the same manner as the first, except that the magnet is held at a sufficient distance to lift the material and not rub among the particles. The magnetic material thus obtained is weighed and sulphur determined in one-half to one gram. The percentage of sulphur existing as pyrrhotite is then calculated from the results by multiplying the percentage of magnetic material found in the ore by the amount of sulphur found in 1 gram of the same. The difficulties in working this method are no doubt apparent to all who have used it. Pyrrhotite is only slightly magnetic and is very difficult to separate from the non-magnetic ore. After following out the method just described with the greatest care it is impossible to remove all the pyrrhotite or to have the magnetic material free from pyrites. We have slightly improved the method in this laboratory by substituting the electromagnet for the ordinary style, but the results are still far from satisfactory.

The method which I am about to describe was worked out in this laboratory, and is based on the solubility of the two sulphides ( $\text{FeS}_2$  and  $\text{Fe}_7\text{S}_8$ ) in hydrochloric acid,  $\text{FeS}_2$  having been found to be practically insoluble while  $\text{Fe}_7\text{S}_8$  seems to be wholly decomposed.

*Details of the Process.*—Determine total sulphur and silica by the usual methods; also copper, zinc, etc., if they are present in appreciable amounts. Test for pyrrhotite with magnet, and if present proceed as follows :

Treat 2 grams of the sample (ground to pass a 100-mesh sieve) in an 8-oz. beaker, covered with a watch-glass, with 30 cc. concentrated hydrochloric acid, boil ten minutes, filter on a weighed Gooch crucible, wash successively with warm dilute hydrochloric acid, hot water, alcohol, and finally several times with small portions of carbon disulphide. Dry at  $100^{\circ}$  and weigh. Weight of residue =  $\text{FeS}_2 + \text{SiO}_2$ .  $(\text{FeS}_2 + \text{SiO}_2) - \text{SiO}_2 = \text{FeS}_2$ . The sulphur required to satisfy the iron in the resulting  $\text{FeS}_2$  is subtracted from the total sulphur, and the remaining sulphur calculated to  $\text{Fe}_7\text{S}_8$  (pyrrhotite). The details of the calculations are as follows :  $\text{FeS}_2 \times 0.534 = \text{sulphur in FeS}_2$ ; subtract this from the total sulphur and multiply the result by factor 2.529; this gives the percentage  $\text{Fe}_7\text{S}_8$  present in the ore. These calculations apply to ores containing only traces of other metals besides iron. If other metals are present in appreciable amounts due allowance will have to be made. Zinc sulphide will be practically all decomposed by the hydrochloric acid; the percentage of zinc found, will therefore have to be satisfied with the required amount of sulphur, and the sulphur thus used deducted from the total sulphur before other calculations are made. Chalcopyrite, on the other hand, is only partly decomposed by the treatment with hydrochloric acid. Thus for the accurate estimation of pyrrhotite it will be necessary to make copper determinations both in the residue and filtrate, and calculate the results to chalcopyrite, subtract the amount of chalcopyrite found in the residue from the total residue, and the amount of sulphur required to satisfy the percentage of copper in the filtrate from the total sulphur before making the calculations. If only a small percentage of copper is present with no other metals, approximate results may be obtained by using dilute acid (1 to 1) for treating the ore. The amount of copper dissolved out by this treatment will be so small that it may be overlooked in the determination. The whole percentage of copper in the ore is in this case calculated to  $\text{CuFeS}_2$ , and deducted from the total residue. Copper may be determined very quickly and

accurately by the cyanide process as described by Ricketts and Miller. If other disturbing factors are present the method will have to be modified accordingly, but the method as described gives results sufficiently accurate for all practical purposes on the great majority of commercial pyrites ores. This process is simple, reasonably quick, and gives much more satisfactory results than the other methods we have tried.

Mr. S. H. Sheib who is connected with this laboratory has rendered valuable assistance in perfecting this method of pyrrhotite determination, and its success is largely due to his careful work.

LABORATORY VIRGINIA-CAROLINA CHEMICAL CO.,  
August 1, 1900.

## THE ESTIMATION OF FAT IN SWEETENED CONDENSED MILK.<sup>1</sup>

BY JOSEPH F. GEISLER.

Received August 8, 1900.

**C**ONDENSED milk, as its name indicates, is a more or less concentrated milk, prepared by evaporating or distilling off a large percentage of the water of the milk. The concentration is usually carried to a degree to meet popular taste and trade requirements, unless the law establishes a specified degree of condensation. Broadly, this class of milk may be divided into the sweetened and unsweetened condensed milk, the former containing a large per cent. of cane-sugar as sweetener and preservative. Aside from its general good qualities, the extreme precaution of cleanliness in the preparation of most of the condensed milks has added much to their popularity, so that the sale and consumption of these milks is assuming vast and rapidly increasing proportions. As an article of food it is therefore more frequently being made the subject of analytical inquiry to determine its quality and freedom from adulteration.

While certain manufacturers pride themselves in turning out a product of uniform color, consistency, and superior keeping qualities and purity, others have deliberately put adulterated goods on the market and were prosecuted and fined for the same.

The analysis of ordinary milk presents no particular difficulties

<sup>1</sup> Read at the Twenty-first General Meeting of the American Chemical Society, June, 1900.

to the experienced analyst, but there is an abundant and cumulative evidence to show that the correct analysis of sweetened condensed milk is difficult and has proved to be a stumbling block to the efforts of many chemists.

Thus, quite recently, an article "A Method of Analysis for Canned Condensed Milk,"<sup>1</sup> by F. S. Hyde, appeared as a "Contribution from the Havemeyer Laboratories of Columbia University, No. 6," and this article has obtained wide circulation.

The results of the analyses of the first 17 samples reported are so utterly out of harmony with the composition of commercial condensed milk that experienced analysts have only to refer to the method whereby the results were obtained to learn the cause of the faulty statements. It is the general experience that the easiest part of analytical work is the writing out of a method. Without going into the details of the article referred to, I would quote<sup>2</sup> the following, which has a decided bearing in the application of the food laws:

A law of New York State requires that no "condensed milk shall be made,—unless the proportion of milk solids shall be in quantity the equivalent of twelve per centum of milk solids in crude milk and of which solids twenty-five per centum shall be fats." Sec. 25, Chap. 143, L. 1894.

"Generally the amount of fat in condensed milk is less than ten per cent. of the whole, or less than twenty-five per cent. of the forty per cent. (more or less) milk solids of which the fat is a part.

"The original cow's milk used may be considerably above the legal standard and yet the degree of condensation be insufficient to bring the manufactured article within the requirements of the law. Under such conditions the manufacturer might be liable to prosecution, although the product might be perfectly wholesome."

In the writer's experience it is the rare exception rather than the rule for condensed milks to contain less than a proportion of 25 per cent. of fat in the milk solids.

If, as stated, milk above the standard required by law be used

<sup>1</sup> This Journal, 21, 439 (1899).

<sup>2</sup> *Ibid.*, 21, 444 (1899).

for the condensation, there could be no legal prosecution of a manufacturer since the concentration would not materially alter the ratio of fat to milk solids, and the section of law quoted does not define the degree of concentration. Therefore, whether condensed little or much, the "condensed" product would not be an infraction of the law quoted, and prosecution under the same is out of the question.

Aside from insufficient condensation, it is generally assumed that skimming or the removal of butter-fat is the principal temptation to defraud on the part of the manufacturer. To prove skimming, the first essential is the accurate estimation of the fat, assuming the per cent. of fat obtained to be butter-fat. That is to say, the mere finding of the required per cent. of fat, and ratio of fat to milk solids would not prove such milk unadulterated unless the fat found was actually butter-fat.

Attempts have been made to remove the butter-fat and substitute other fat for the same in condensed milk; hence, the allusion to butter-fat particularly.

In the unsweetened condensed milk the estimation of the fat presents no particular difficulty, especially since the introduction of the Adams' coil method,<sup>1</sup> when the necessary precautions are taken. The large surface over which the milk solids are spread in the paper, a minimum of 110 sq. in., offers a medium from which solvents ordinarily rapidly extract<sup>2</sup> the fat.

The coil method has found general favor among analysts and were it not for the inconvenience of preparing "fat-free" coils it would be *par excellence*, and with certain modifications, the best method for the purpose. The preparation of the coils is tedious, but where accuracy is required the previous extracting of the coils to be used must be resorted to, as the quality of paper varies, some lots containing considerably more extractable matter than others.

Chemists were quick to avail themselves of the advantages of the coil method and use it in the estimation of fat in sweetened condensed milk, for the large surface offered advantages to overcome the difficulties experienced and pointed out by Hehner,<sup>3</sup>

<sup>1</sup> *Analyst*, March, 1885.

<sup>2</sup> See Vleth : *Analyst*, 16, 127; Geisler : "The Relative Merits of the Wanklyn and the Adams Methods in the Estimation of Fat in Milk Analysis," this Journal, 12, 488-500.

<sup>3</sup> *Analyst*, 4, 45 (1879).

who stated "that it is quite impossible to extract the fat from the total solids by means of ether, or benzoline, the large amount of cane-sugar effectually protecting the fat."

Adams' method was not available until some years later. In the light of recent published analyses of sweetened condensed milk, Hehner was a "martyr" considering the abuse heaped on him by the manufacturers for the analyses, for it will presently be shown that even the extreme advantages of the *coil method*, unless certain precautions are taken, has its pitfalls. In the application of the coil method it is customary among a large number of chemists to proceed as follows: Thus Cornwall<sup>1</sup> and Wallace<sup>2</sup> state in following out the method:

"Rather thick, white filter-paper was thoroughly extracted with ether in a Soxhlet apparatus and 5 cc. of the diluted milk (equal to 2 grams of the condensed milk) dropped on a nearly square strip of this paper<sup>3</sup> large enough to conveniently soak up the milk. To avoid the formation of candied spots the milk was uniformly spread over the paper by brushing with a small narrow strip of the same kind of paper. After drying in the air the paper was rolled into a loose cylinder and dried in the air-bath at 100° C. for about an hour and a half.

"The fat was then extracted with ether, for two hours, in a Soxhlet apparatus, and a second extraction was made, lasting for an hour to an hour and a half longer. The second extraction usually yielded less than 4 milligrams more of fat, and often none at all. The fat determination was made in duplicate. The greatest difference was 0.2 per cent., usually only a hundredth of a per cent."

In brief, the Adams' method, as applied to sweetened condensed milk, consists in transferring about 2 grams of milk diluted to 5 or 6 cc., to a paper coil of 50–60 sq. in. (100–120 sq. in. of surface, both sides), and extracting the fat by means of ether or petroleum ether.

The quantity of milk taken for the extraction is not a matter

<sup>1</sup> Cornwall: Rep. Dairy Com., N. Y. State, 1890, p. 408; N. J., 1887.

<sup>2</sup> Wallace: Rep. Dairy Com., N. J., 1899, pp. 43–47.

<sup>3</sup> Cornwall: Rep. Dairy Com., N. J., 1891, p. 90; filter-paper of medium thickness 10 × 5 inches. Wiley: Rep. Dairy Com., N. J., 1891; thick filter-paper strips 24 × 2 inches.

of indifference, nor is the solvent, or the method of extraction. Unless the ether is dry and free from alcohol, the coils get too soggy to permit the full extraction of the fat. Even with dry ether or petroleum ether, losses may occur even as high as 0.5 per cent. as against an occasional maximum of about 1 per cent. in a direct extraction: Evidence of this may be obtained by treating the thoroughly exhausted coil after drying, to a thorough soaking in water until all soluble matter is removed, drying the coil, and again exhausting with ether or petroleum ether, when additional fat will be found in the majority of cases.

Direct exhaustion by ether for four hours leaves variable percentages of fat in the residuum on the coils. This is true of other solvents as well. If 2 grams of the condensed milk are used per coil, the coil, after the first exhaustion, which presumably should yield all the fat, should be dried and exhausted with water, again dried and exhausted with the volatile solvent. Forty-nine separate examinations showed differences for the second exhaustion of 0.27 to 1.2 per cent. of which nine ranged from 0.27 to 0.49 per cent. ; twenty-three from 0.50 to 0.75 per cent. ; and the remainder from 0.75 to 1.2 per cent. That is to say, if the precaution of exhausting the coils with water had not been taken, the fat in the milks would have been underestimated from 0.27 to 1.2 per cent. in actual per cent. of fat by the coil method.

The large variation is due principally to the varying per cent. of cane-sugar in the different samples. As the time of extraction for these varied from two and a half to four hours for the first extraction, a separate set of extractions under fixed conditions was made. The coils (filter-paper strips  $22 \times 2.5$  inches, were "alcohol-ether" coils, and each coil again exhausted for five hours with the solvent with which it was to be subsequently treated. Simple exhaustion of the coils by ether alone does not remove all the extractable matter from the same. The extractive matter obtained for the eight individual coils varied from 1 milligram to a maximum of 2.5 milligrams. The latter was extracted by petroleum ether from a coil not previously treated with this solvent.

The eight coils were therefore free from extractable matter. Two were taken to be extracted with petroleum ether, and two with a mixture of petroleum ether (15 per cent.) and ethyl ether. The first extraction lasted three hours and the second two hours.

After the first three hours' exhaustion, the coils were taken out and dried, and then exhausted with water until all soluble matter was removed. The coils were again dried and again subjected to their respective solvents for two hours. The results obtained were as follows :

**PETROLEUM ETHER.**

Amount taken. Grams.		Fat. Gram.	Per cent.
2.0355	First extraction.....	0.160	7.86
	Second " .....	0.013	0.63
			<hr/> 8.49
2.0815	First extraction.....	0.158	7.59
	Second " .....	0.015	0.72
			<hr/> 8.31 <sup>1</sup>

**" ETHER-PETROLEUM" ETHER.**

Amount taken. Grams.		Fat. Gram.	Per cent.
2.0645	First extraction.....	0.156	7.55
	Second " .....	0.017	0.82
			<hr/> 8.37
2.035	First extraction.....	0.1605	7.88
	Second " .....	0.012	0.58
			<hr/> 8.46

Results by taking about 1 gram of milk and treating as above:

1.0235 grams taken gave 0.0854 gram fat or 8.35 per cent.

1.084 grams taken gave 0.0917 gram fat or 8.46 per cent.

Direct exhaustion with petroleum ether for five hours for the first exhaustion, and two hours further exhaustion after the water treatment, gave :

Amount taken. Grams.		Fat. Gram.	Per cent.
2.0395	First extraction.....	0.159	7.795
	Second " .....	0.0135	0.661
			<hr/> 8.456
2.013	First extraction.....	0.155	7.699
	Second " .....	0.0155	0.769
			<hr/> 8.468

The actual time limit will not in all cases do justice to extraction where petroleum ether is used to any extent, as the siphonings are

<sup>1</sup> Water slightly milky, indicating loss of fat.



not always regular. Anhydrous ether, *i. e.*, water-washed ether shaken with concentrated glycerine and redistilled after separation has taken place, shows differences as great as those. The mixture of petroleum ether and ethyl ether was a water-washed ethyl ether mixed with 15 per cent. of petroleum ether prepared by thoroughly shaking and mixing the mixed ether with about 25 per cent. of concentrated glycerine and redistilling the thoroughly separated ether mixture. Coils treated with an anhydrous ether are usually quite crisp when taken out of the extraction apparatus.

Chemists who have made comparative tests have no doubt found that 1 gram of the condensed milk per coil will usually yield all the fat to within 0.2 to 0.3 per cent. on four or five hours' extraction with petroleum ether, or dry ethyl ether, or a mixture of ethyl and petroleum ether, and that the loss rarely exceeds 0.2 per cent.

The amount of milk<sup>1</sup> used per coil is quite a variable one among chemists.

The method of taking a sample and transferring it to the coil may be minor details but important as to possible variation in results by the coil method. While the quantity of original milk will be noticed to vary from 0.5 to 2 grams per coil, it must be apparent that the margin of safety may be overstepped in either direction, for while the maximum quantity may be too large for complete direct extraction, the minimum quantity is too small, as a difference of 1 milligram in fat obtained represents at once 0.2 per cent. For the general run of fat estimation, little fault will be found with results obtained by exhausting the fat from 1 gram of the condensed milk from a *fat-free* coil by the direct exhaustion for four to five hours with petroleum ether, or ether-petroleum ether.

Accuracy in fat estimation to within 0.2 per cent. in sweetened condensed milk is certainly attainable where the necessary precautions are taken. Where 2 grams of the condensed milk are taken the results cannot be depended upon, however, as repre-

<sup>1</sup> T. H. Pearman and C. G. Moor (*Analyst*, 20, 268) use 5 cc. of a 10 per cent. solution; A. H. Allen ("Commercial Organic Analysis," Vol. IV., 2nd ed., p. 235) recommends 5 cc. of a 10 per cent. solution; J. H. Shenstone (*Analyst*, 13, 222) uses 2 grams; Wallace (N. J. State Dairy Com. Rep., 1899, pp. 43-47) uses 2 grams; Cornwall (N. J. State Dairy Com. Rep., 1887, 1890, p. 408) uses 2 grams; H. Throop Richmond and L. K. Boseley (*Analyst*, 18, 170) use 5 cc. of a 15-30 per cent. solution.

senting the full yield of fat, unless the exhausted and dried coil is exhausted with water, and again exhausted with the volatile solvent. Water-washed ether mixed with 10 to 15 per cent. petroleum ether and distilled after shaking out with concentrated glycerine, answers the purpose as well as petroleum ether, as a solvent, and possesses other advantages if the petroleum ether has the proper boiling-point. The commercial petroleum ether is not suitable for this purpose, but suitable fractions of the same may readily be obtained on distillation.

The effective manner in which the cane-sugar prevents the action of the solvents upon the fat is well illustrated in the asbestos-tube method for fat estimation, in which 20 cc. of a 20 per cent. solution of the milk (4 grams) is deposited upon asbestos fiber, and, after drying, exhausted with petroleum ether. This method<sup>1</sup> has been the means of the unjust and unwarranted condemnation of quite a number of condensed milks. It has been proved that the method failed to exhaust all the fat, often 2 to 3 per cent. remaining in the residue, as has been amply demonstrated by exhausting the residue with water and recovering the shortage of fat in the residuum. The asbestos method has found favor in many quarters and was the direct cause of condemnation of pure milks in several instances.

The recurring frequency of unjust condemnation of condensed milk makes it particularly necessary for chemists to exercise great caution in expressing opinions upon whether a milk is skimmed or not. There are instances on record where sweetened condensed milks with high content of cane-sugar and of unquestioned purity were condemned as adulterated on the strength of the analysts finding low percentages of fat (3.8 per cent. lowest and a considerable number ranging from 5.5 to 6.8 per cent.) when more accurate methods demonstrated the presence of over 8 per cent. of fat in all the samples.

A difference of 0.5 per cent. fat has a very important bearing in the enforcement of a law defining the fat contents in milk solids. This is particularly true when the Ritthausen method is used for the estimation of the albuminoids, any error in the fat estimation reflecting its deficiency in increase of the albuminoids (the albuminoids being determined by difference) so that the

<sup>1</sup> Bulletin No. 54. Condensed Milk, Inland Revenue Department, Canada.

ratio between fat and albuminoid is distorted to a degree which would reflect seriously upon the milk under examination, and indicate probable skimming in the minds of some chemists.

This no doubt accounts for the discrepancy in quite a number of published analyses of the excess of albuminoid over fat in what probably were unskimmed milks. When such discrepancies are noticed in an analysis it is advisable to check the results by a nitrogen estimation by the Kjeldahl method, if this was not used in the first instance.

#### CONCLUSION.

In conclusion I would add that where as much as 2 grams of the sweetened condensed milk is used per "Adams' coil," the full extraction of the fats cannot be depended upon in a direct exhaustion of the coil by a four or five hours' treatment. For general usage 1 gram of milk per *fat-free* coil and four or five hours' exhaustion will give results which will rarely exceed the experimental errors common to complicated methods in which many minor details all must add their perceptible quota to a final result. The asbestos-tube<sup>1</sup> method, without water exhaustion, cannot be considered as giving acceptable results, as the shortage of fat by the same renders the results worthless. Three or four hours' exhaustion of the dried residue with petroleum ether, drying the exhausted mass and reexhausting with petroleum ether, will recover most of the fat.

The details of *modus operandi* especially as to proportion of milk taken to asbestos can no doubt be adjusted so that with the precaution of water exhaustion indicated the results will be fully as reliable as those by other methods. The many factors entering into any method for fat estimation in sweetened condensed milk would indicate that maximum variations of  $\pm 0.1$  are possible, and that any method yielding uniform results within that range would be acceptable for all ordinary purposes, as to accuracy.

<sup>1</sup> Bulletin No. 54, Condensed Milk, Inland Rev. Dep't, Canada.

## A NEW COAL CALORIMETER.

BY S. W. PARR.

Received July 24, 1900.

**I**N the study of combustibles and in all tests connected with fuels no data is of any value that does not go back to the thermal units involved. This fact itself is not new but its application, especially in technical work, has had a marked increase in recent years. This increase has come about in spite of, rather than because of, the instruments available for the determination of heat units. It is not necessary here to describe the difficulties and defects connected with existing calorimeters, more than to note perhaps the two extremes; *viz.*, the L. Thompson calorimeter on the one hand which admits of results varying by 15 per cent. from the truth, and the high pressure bomb on the other which, while accurate, requires an elaboration of apparatus and skill in manipulation not conducive to the wide use it deserves.

The calorimeter here described has the advantage of operating without an oxygen gas supply; its manipulation is simple and the extraction of the heat rapid, owing to the compact mass in which the heat is generated. It is especially adapted to soft coal and while designed for technical purposes its factor of error is well within 0.5 per cent., making its results, therefore, easily comparable with those obtained by the Berthelot or Mahler bombs. The principle involved in the process depends upon the liberation of oxygen from such a compound or chemical as shall in turn absorb the products of combustion thereby avoiding the necessity of providing conduits for the gases. A chemical which admirably meets these requirements is sodium peroxide. Its operation may be illustrated by the following experiment which was one of the first used to determine the adaptability of this chemical. A sample of combustible and sodium peroxide in suitable proportion were placed in a short, heavy, copper tube with close-fitting screw plugs at each end and the contents thoroughly mixed by shaking. The bomb was then held in the flame of a Bunsen burner till ignition was effected. Upon cooling and opening it was found that no pressure of gas was pres-

ent and on dissolving out the fused mass the combustion was shown to be complete. The instrument ultimately employed for utilizing these conditions may be best shown by an outline sketch.

A (Fig. 1) is a copper vessel of a little over two liters' capacity insulated by two outer vessels of indurated fiber, B and C, so

Fig. 1.

placed as to provide further insulation by the air spaces *b* and *c*. The cover is double to correspond with an air space between, the two parts being connected for convenience in handling. The cartridge D has an inside capacity of about 25 cc. It rests on a pivot below and extends through the covers above and has a small removable pulley at the end. Turbine wings fastened to spring clips are placed on the cartridge, and a short cylinder E, open at both ends, is provided for directing the current set up

by rotation of the vanes attached to the cartridge. The vanes are so set as to deflect the currents downward first along the cartridge and then up along the outside of the cylinder. The stem G of the cartridge is so arranged as to permit the passage of a short piece of No. 12 copper wire (Fig. 2). It is, moreover, pro-

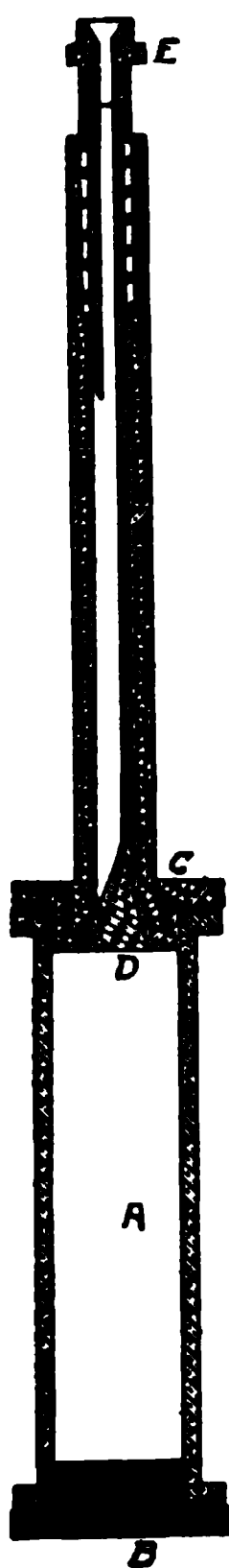


Fig. 2.

vided with a valve D at the lower end which prevents the escape of the enclosed air when heated by the combustion of the charge. The two ends B and C of the cartridge screw on. The process then is as follows: 1 gram of coal ground to pass through a 100-mesh sieve and dried in the oven as usual at  $105^{\circ}$ – $110^{\circ}$  is put into the cartridge, 16 to 18 grams of sodium peroxide are added, the top screwed on and the whole shaken to thoroughly mix the contents. The peroxide varies somewhat in fineness. It should practically all pass through a 25-mesh or 1 mm. sieve. After tapping the cartridge to settle the charge in the bottom, it is placed in the can and 2 liters of water added, the temperature of the water being  $3^{\circ}$  or  $4^{\circ}$  lower than the temperature of the work room. The pulley is connected by string to a small water or electrical motor giving about 50 to 100 revolutions per minute to the cartridge. When constant temperature is reached, the reading of the thermometer is taken and the hot wire is dropped through the valve into the charge which is at once ignited and burns completely in two or three seconds. The extraction of the heat is effected in about five minutes. The reading of the maximum temperature is taken and the calculations made as follows :

*First.*—A correction factor is needed for the hot wire. The average of many determinations on various lengths up to 2 inches establishes a fairly uniform factor of  $0.012^{\circ}$  C. or  $0.021^{\circ}$  F. per  $\frac{1}{2}$  inch of No. 12 copper wire. In this work the lengths used have been  $\frac{1}{4}$  inch and  $\frac{3}{8}$  inch and the correction factor for the wire has been  $0.006^{\circ}$  and  $0.009^{\circ}$ .

*Second.*—A correction is made necessary by reason of the heat resulting from the combination of the products of combustion, carbon dioxide and water, with the chemical employed. This

heat of combination causes an excess over and above the actual heat of combustion, amounting to 27 per cent. of the total indicated heat. Hence, this correction must also be applied in the calculation. The method then of calculation will be as follows: Supposing a centigrade scale to have been used, if  $C'$  represents the total indicated calories,  $C$  the actual calories due to combustion,  $t$  the rise in temperature, and  $w$  the water employed,

then 
$$C' = (t - 0.012^\circ) \times w,$$

and 
$$C = C' - \frac{C' \times 27}{100},$$

or 
$$C = (t - 0.012^\circ) \times w \times 0.73.$$

In case a Fahrenheit thermometer is used the temperature of correction for  $\frac{1}{2}$  inch of wire is  $0.021^\circ$  instead of  $0.012^\circ$  and the final result is B. T. U. per pound of coal instead of calories. Of course with a centigrade thermometer the ultimate reading is changed from calories to B. T. U. by multiplying the calories obtained by 1.8.

A word of explanation is necessary as to the method of arriving at the factor for the heat of absorption of the products of combustion. The two elements concerned are carbon and hydrogen. For the carbon dioxide resulting from the combustion of the former, the correction factor is easily determined. Pure sugar carbon is prepared and run in the calorimeter as above described. The average of a number of such determinations gave a total calorific result of 11,084. Now taking as the accepted figure for the heat of combustion of carbon in calories, 8,080, we have therefore an increase of 3,004 calories due to the heat of absorption of the carbon dioxide by the chemical. By computation this is found to be 27.1 per cent. of the total indicated heat. Now as to the heat due to the absorption of water from the combustion of hydrogen the problem is not so simple. The burning of sugar affords no indication, for seemingly other compounds than water are formed and as in the case of sugar burned in the bomb calorimeter, while the results are constant and repeat themselves with exactness, they vary so widely from the theoretical data as to make it evident that the combinations do not proceed in a simple manner. Naphthalene does not afford a factor, chiefly owing to its volatility and consequent

faulty combustion. The liberation of a known weight of water in the interior of the cartridge gave very indifferent results, the water not disseminating throughout the peroxide but incrusting itself in a moist mass. Many other methods were tried with the result that so far at least it has been necessary to fall back on empirical data obtained from burning widely different varieties of coals and checking the same coals by combustion in standard bomb calorimeters. The following table gives the results thus obtained, using coals varying in their ash content from 3 to 32 per cent., and in water from 1 to 14 per cent. Also as wide a variation in the character of their hydrocarbons as possible, using a cannel coal,—Pennsylvania gas coal, a lignite and soft coals from widely separated districts in Illinois. Supposing the factor for absorption of water formed from a given weight of hydrogen to be approximately the same per cent. of total heat evolved as in the case of carbon dioxide, *viz.*, 27 per cent. and applying this factor throughout, we have the following results obtained by running parallel combustions in a standard Atwater or Mahler bomb calorimeter and the sodium peroxide apparatus. In a number of samples the process was conducted in both the Atwater and Mahler bombs. The instruments, however, checked so closely that this practice was not continued throughout the tests. The proximate analysis is included in the table in order that the wide variations in the character of the coals may be indicated (see table).

A few facts should be noted :

(a) It has been discovered after most tedious experience that a comparison of calorimeters should be made at approximately the same time. For example a series of calorific determinations made on finely ground samples on May 12, 1900, were found to give a reading 2.4 per cent. less on July 12, 1900. It was necessary to repeat practically all the above determinations on this account, all results showing a slow deterioration in the finely ground samples. This subject will receive further attention later.

(b) In the table it should be noted that the first five samples are from the same mine and vary but slightly in composition. The particular purpose in introducing this series was to note if



## A NEW COAL CALORIMETER.

Kind of coal.	Proximate analysis.					B. T. U. per pound air-dried coal.		Variation from standard bomb in per cent.
	Moisture.	Volatile combustible.	Fixed carbon.	Ash.	Sulphur.	Bomb calorimeter.	New method.	
216 Cartersville, Ill., mine run.....	4.87	34.11	52.17	8.85	0.85	12,205	12,214	+0.07
217 " " washed No. 1.....	4.66	33.99	54.21	7.14	0.74	12,289	12,286	0.00
218 " " " 2.....	4.31	35.12	55.01	5.56	0.87	12,914	12,934	+0.08
220 " " " 4.....	4.86	33.26	55.29	6.59	1.15	12,355	12,345	-0.08
221 " " dust from washer.....	5.50	32.97	53.01	8.52	1.16	12,384	12,336	-0.39
226 Odin, Ill., pea coal .....	7.27	35.76	42.96	14.01	3.89	11,025	11,064	+0.35
227 Farmington, Ill., mine run .....	11.22	35.93	36.60	16.25	3.98	9,986	10,018	+0.32
228 Pennsylvania gas coal .....	0.92	36.66	58.94	3.46	1.40	14,270	14,275	0.00
229 Kentucky cannel coal.....	0.99	32.33	34.35	32.33	1.07	10,313	10,328	+0.14
230 Mississippi lignite.....	14.56	43.82	29.30	12.32	...	8,316	8,378	+0.74

the calorimeter would differentiate between such small variations in the inert material, the ash and water.

Tabulating the results with reference to these inert materials and giving simply the calorimetric reading for each we have :

No.	Total of water and ash. Per cent.	B. T. U.
216	13.79	12,214
217	11.80	12,286
218	9.87	12,924
220	11.45	12,345
221	14.02	12,056

(c) It has already been mentioned but attention should again be called to the fact that with the calorimeter it is necessary to operate on the oven-dried sample for the reason that the water, if left in the sample, gives off heat in combining with the chemical; hence, a gram sample is weighed and dried in the oven or if the per cent. of moisture is known, an oven-dried sample may be weighed out, making allowance for the water. No other conditions vary the results. About 17 times the weight of coal is the best amount of peroxide to insure complete combustion but variations from 16 to 20 times the amount do not appreciably vary the results. Indeed with careful work and a good thermometer the instrument repeats its own results fully as closely as the bomb calorimeters. The usual practice, moreover, has been to work with half-gram samples, using a measured quantity,—8 to 9 grams of peroxide. With a suitable room and reasonable precautions as to temperature of both room and water employed, exceedingly constant and satisfactory results may be obtained which should vary less than 0.5 per cent. from the best figure obtainable with a standard instrument.

UNIVERSITY OF ILLINOIS,  
URBANA, ILL.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA  
UNIVERSITY, No. 28.]

## ON THE DETERMINATION OF PHOSPHORIC ACID AS PHOSPHOMOLYBDIC ANHYDRIDE.

BY H. C. SHERMAN AND HENRY ST. JOHN HYDE.

Received July 23, 1900.

**A**LTHOUGH a great amount of work has been done in this country upon the subject of phosphorus determination, practically no attention seems to have been given to methods

which involve the ignition of ammonium phosphomolybdate and weighing of the residue. A given weight of phosphoric acid yields about sixteen times as much phosphomolybdic anhydride as magnesium pyrophosphate, and the "yellow precipitate can be ignited much more quickly and apparently with quite as definite results as it can be dried. It seems strange, therefore, that less attention has been given to this than to the other rapid gravimetric methods.

The first attempt to determine phosphoric acid as phosphomolybdic anhydride was probably that of Meineke.<sup>1</sup> The phosphate was precipitated by means of the ordinary acid molybdate reagent from a solution containing 20 to 25 per cent. of ammonium nitrate, heated to 50°–60° and vigorously stirred. After washing with a weakly acid solution of ammonium nitrate, the precipitate was heated below redness for fifteen minutes. The residue was believed to be of constant composition and to it was assigned the formula  $P_2O_5 \cdot Mo_{24}O_{68}$ .

Hanamann<sup>2</sup> about ten years later published a method very similar to that of Meineke but recommended that the precipitation be made at room temperature.

Later Meineke<sup>3</sup> made an extended series of determinations on solutions of pure phosphates from the average of which he calculated the percentage of  $P_2O_5$  in the residue to be 3.949 per cent., agreeing well with the formula,  $P_2O_5 \cdot 24MoO_3$ . He recommended that in the presence of a little iron the precipitation be carried out at 50° in the presence of 5 per cent. of ammonium nitrate, using the ordinary acid molybdate solution while if the solution contained much iron at least 10 per cent. of ammonium nitrate and 5 to 10 per cent. of strong nitric acid should be present and the precipitation carried out at a higher temperature. Good results are reported on two samples of phosphate.

Woy<sup>4</sup> developed the following method and applied it to a variety of technical products:

*Reagents.*—(1) A 3 per cent. solution of ammonium molybdate; (2) ammonium nitrate solution—340 grams per liter; (3) nitric acid of 1.153 sp. gr.; (4) wash solution containing

<sup>1</sup> *Repert. anal. Chem.*, 8, 153 (1885); *Ztschr. anal. Chem.*, 26, 636 (1887).

<sup>2</sup> *Chem. Ztg.*, 19, 553 (1895).

<sup>3</sup> *Ibid.*, 20, 108 (1896).

<sup>4</sup> *Ibid.*, 21, 441 and 469 (1897).

200 grams ammonium nitrate and 160 cc. of nitric acid in 4 liters of water.

*Procedure.*—To an aliquot part of the solution corresponding to 0.5 gram substance, add 30 cc. ammonium nitrate solution and 10 to 20 cc. of the nitric acid and heat until bubbles commence to rise, then add the necessary quantity of molybdate solution heated to the same degree (about 80° in our experiments). The reagent is run into the middle of the solution which is kept in motion during the operation. After fifteen minutes when the precipitate has settled, the solution is decanted through a porcelain Gooch crucible, the precipitate washed by decantation with 50 cc. of the wash solution and then dissolved in the beaker in dilute ammonia and reprecipitated by adding hot nitric acid, drop by drop, stirring or shaking the solution. Filter on the porcelain Gooch crucible and wash with the hot wash solution. Finally place the porcelain crucible inside of a nickel crucible and heat until the bottom of the latter is dull red. After fifteen minutes the precipitate is transformed into  $P_2O_5 \cdot 24MoO_3$ .

Pellet<sup>1</sup> considers the second precipitation of ammonium phosphomolybdate recommended by Woy to be unnecessary. Having seen only a brief abstract of his paper we do not know the nature of the experiments on which his conclusion is based.

Hanamann<sup>2</sup> suggests that contamination with silica is best avoided by carrying out the precipitation at a low temperature and in the presence of considerable free nitric acid.

Some preliminary trials with microcosmic salt solutions having given results quite favorable to Woy's method whether with or without a second precipitation, we were led to compare on a number of samples: (1) The well-known molybdate-magnesia method carried out according to the directions of the Association of Official Agricultural Chemists and here called the official method; (2) Woy's method as published; (3) Woy's method, omitting the second precipitation of ammonium phosphomolybdate. The samples tested were not only "mixed" fertilizers but nearly all of them were "composites" so that together they represent a large variety of fertilizer materials.

<sup>1</sup> *Rev. Chim. Analyt. Appl.*, v. (20), 405; *Abs. Analyst*, 23, 25 (1898).

<sup>2</sup> *Ztschr. landw. Vers-Sta. Ost.*, 3, 53; *Abs. J. Soc. Chem. Ind.*, 378 (1900).

In each case solution was effected by boiling with 30 to 50 cc. of concentrated nitric acid and 5 to 10 cc. concentrated hydrochloric acid. The organic matter was not burned off before the solution nor was the silica removed by evaporation. The results obtained are shown in Table A which follows :

TABLE A. RESULTS WITH AND WITHOUT REPRECIPITATION.

No.	Description of sample.	Official method. Per cent. P <sub>2</sub> O <sub>5</sub> .	Woy's method	
			as published. Per cent. P <sub>2</sub> O <sub>5</sub> .	omitting 2nd precipitation. Per cent. P <sub>2</sub> O <sub>5</sub> .
1.	Mixed fertilizer	..... 11.16	11.13	11.16
2.	" "	..... 12.23	12.26	12.27
3.	" "	..... 12.95	12.84	13.02
4.	" "	..... 11.15	11.26	11.11
5.	" "	..... 9.80	9.73	9.60
6.	" "	..... 10.84	10.95	10.93
7.	" "	..... 10.53	10.62	10.70
Average .....		11.24	11.26	11.26

In these samples the second precipitation demanded by Woy's method seems to have been entirely unnecessary. We therefore tried the effects of salts of a few of the commoner acids and bases upon the results obtained by ignition of the first yellow precipitate. A commercial superphosphate was dissolved as above and its phosphoric acid content determined by the official method and by ignition of the first "yellow" precipitate. To aliquot parts of the same solution, corresponding to 0.4 gram of substance, were added the various salts, about 0.4 gram being used in each case. The yellow precipitate was ignited without reprecipitation. The determinations were not duplicated as in no case was the deviation from the true percentage greater than might easily be due to manipulation of a new method. The results are shown in Table B.

TABLE B. EFFECTS OF IMPURITIES.

Sample.	Method.	Per cent. P <sub>2</sub> O <sub>5</sub> .	Average.
Superphosphate.	Official method.	18.26	.....
"	Ignition of first yellow ppt.	18.14	18.20
" + NaNO <sub>3</sub>	" "	18.16	.....
" + KNO <sub>3</sub>	" "	18.10	.....
" + Sr(NO <sub>3</sub> ) <sub>2</sub>	" "	18.31	.....
" + Mg(NO <sub>3</sub> ) <sub>2</sub>	" "	18.21	.....
" + Fe(NO <sub>3</sub> ) <sub>3</sub>	" "	18.15	.....
" + Ba(NO <sub>3</sub> ) <sub>2</sub>	" "	18.33	.....
" + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	" "	18.17	.....
" + NH <sub>4</sub> Cl <sup>1</sup>	" "	18.10	18.19

<sup>1</sup> Woy found that very large quantities of ammonium chloride interfered with the precipitation of ammonium phosphomolybdate.

In carrying out the method it was naturally found that the precipitate formed was more granular and more easily washed if the molybdate solution was added very slowly and with vigorous stirring. The modification which follows seems to us to combine most of the best features of Woy's and Gladding's methods.

#### MODIFIED METHOD.

To the solution representing 0.2 to 0.5 gram of the sample, add 25 cc. strong ammonia (sp. gr. 0.90), neutralize with nitric acid and then add 5 to 8 cc., according to the impurities present, of concentrated nitric acid (sp. gr. 1.42) in excess. Bring the solution to a bulk of about 150 cc. and a temperature of 50° C. and maintain at this temperature (conveniently by standing the beaker in a pan of warm water) while adding, drop by drop with constant stirring, a neutral 3 per cent. solution of ammonium molybdate sufficient to give an excess of about 20 cc. Stir vigorously and allow to stand for about ten minutes; decant through a porcelain Gooch crucible and wash the precipitate three times by decantation with 50 to 70 cc. and then on the filter with 200 to 250 cc. of a cold solution of one part concentrated nitric acid in 100 parts of water. Finally the precipitate is ignited as described by Woy, leaving a residue of  $P_2O_5 \cdot 24MoO_3$ .

Suction was employed in the filtration, and in washing on the filter the precipitate was well stirred up with the dilute acid wash solution. The neutral ammonium molybdate solution was employed simply to permit of the direct addition of the desired amount of nitric acid irrespective of the amount of the molybdate solution to be used.

As would be expected in working any new method, a few individual determinations were found on repetition to be wrong. These "wild" results were too high, doubtless from the precipitation of impurities, and emphasize the necessity of careful, slow addition of the molybdate solution. Only one sample was encountered in which the results obtained by the method described differed by more than two-tenths of one per cent. from those given by the official method. This was a phosphatic slag which contained, according to the official method, 17.27 per

cent. and according to the new method 16.97 per cent. of  $P_2O_5$ . The final precipitate obtained by the official method was, however, contaminated with iron and this result was thus undoubtedly too high, that by the new method being probably nearer the truth. These results on this sample are therefore omitted from the table which follows.

Table C below shows the results obtained by Woy's method, omitting the second precipitation, and by the modified method described above, together with the results obtained by the official method. The samples are numbered in the order in which they were analyzed.

TABLE C. COMPARISON OF RESULTS.

		Per cent. $P_2O_5$ found.		
No.	Description of sample.	Official method.	Woy's method, omitting the second precipitation.	Modification of Woy's method, page 656.
1.	Mixed fertilizer .....	11.16	11.16	.....
2.	“ .....	12.23	12.27	.....
3.	“ .....	12.95	13.02	.....
4.	“ .....	11.15	11.11	.....
5.	“ .....	9.80	9.60	.....
6.	“ .....	10.84	10.93	.....
7.	“ .....	10.53	10.70	.....
8.	Acid phosphate.....	18.26	18.14	.....
9.	Mixed fertilizer .....	14.90	14.91	.....
10.	“ .....	11.21	11.27	.....
11.	“ .....	13.75	13.66	.....
12.	“ .....	11.44	11.54	11.45
13.	“ .....	17.55	17.57	17.42
14.	Steamed raw bone.....	32.34	.....	32.32
15.	Natural soft phosphate .....	20.80	.....	20.92
16.	South Carolina phosphate....	27.60	.....	27.74
17.	Florida phosphate.....	29.76	.....	29.76
18.	South Carolina phosphate....	27.92	.....	27.80
19.	Basic slag phosphate .....	17.77	.....	17.67
	Average, Nos. 1 to 13 .....	12.75	12.76	.....
	Average, Nos. 12 to 19 .....	23.15	.....	23.14

CONCLUSION.

In all of the twenty samples examined, which represent a large

variety of the common phosphatic materials of the fertilizer industry, the determination of phosphoric acid as phosphomolybdic anhydride was found to give satisfactory results even without a reprecipitation of the ammonium phosphomolybdate.

The presence in considerable quantity of some of the common acids and bases was found to be without appreciable effect.

With either modification of the method the average result obtained on all the samples analyzed was practically the same as that yielded by the official method which would seem to indicate that such variations as occur are due mainly to manipulation.

By the method described a determination may be completed in much less time than by any other gravimetric method with which we are familiar but in handling several samples simultaneously, the saving of time is less apparent.

COLUMBIA UNIVERSITY, NEW YORK CITY, July, 1900.

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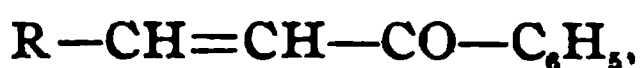
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

## THE ACTION OF SODIUM ALCOHOLATE UPON ANISYLIDENE ACETOPHENONE DIBROMIDE.

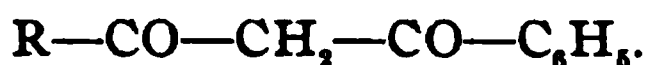
BY F. J. POND AND ARTHUR S. SHOFFSTALL.

Received August 1, 1900.

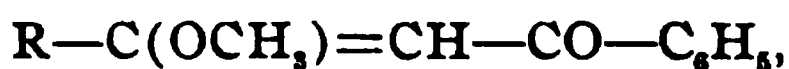
IN a preceding communication<sup>1</sup> on this subject it was mentioned that sodium methyllate reacts with the dibromides of certain unsaturated ketones of the general formula,



yielding 1,3-diketones of the formula,



Thus benzylidene acetophenone dibromide was readily converted into *dibenzoyl methane*, and anisylidene acetophenone dibromide was found to give a 1,3-diketone analogous to dibenzoyl methane, and called *anisoyl benzoyl methane*. It was suggested that the formation of these diketones from the dibromides of unsaturated ketones was accomplished by the production of unsaturated ethers,



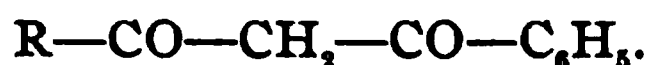
<sup>1</sup> Pond, Maxwell, and Norman: This Journal, 21, 955.



which were converted by hydrolysis with dilute acids into the unsaturated ketone alcohols,

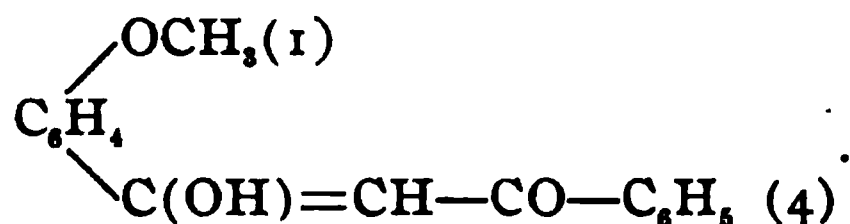


and these, in turn, by an intramolecular change into the saturated 1,3-diketones,

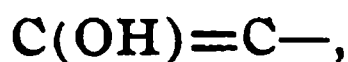


Such a reaction would be somewhat analogous with the formation of ketones from the dibromides of anethol, isosafrol, and other propenyl compounds.

Closer investigation of the compound obtained from anisylidene acetophenone dibromide and of its derivatives leads us to believe that the last-mentioned change of the unsaturated ketone alcohol into the saturated diketone does not take place, and that the compound is a keto-enolic modification of anisoyl benzoyl methane and may be called *α-oxyanisylidene acetophenone*,



Its solution in alcohol is colored an intense brownish red by the addition of ferric chloride; aqueous ferric acetate, made by mixing the solutions of one part of ferric chloride and three parts of sodium acetate, throws out the ferric salt of *α-oxyanisylidene acetophenone* as a brick-red, crystalline precipitate, which is insoluble in water and alcohol, but soluble in dilute hydrochloric acid. W. Wislicenus<sup>1</sup> has suggested that the formation of such colored iron compounds on the addition of ferric chloride to the alcoholic solutions is a property of compounds containing the group,



such as phenols and the enolic modifications of *β*-keto-compounds; also, that in these colored iron compounds the metal is joined to the oxygen atom, a view which Claisen<sup>2</sup> also holds regarding the constitution of the iron salts of the *β*- or 1,3-diketones.

This compound is soluble in dilute alkalies, and is reprecipitated by acids. A green, crystalline copper salt is precipitated from its alcoholic solution by an alcoholic solution of copper ace-

<sup>1</sup> W. Wislicenus: *Ann. Chem. (Liebig)*, 291, 174.

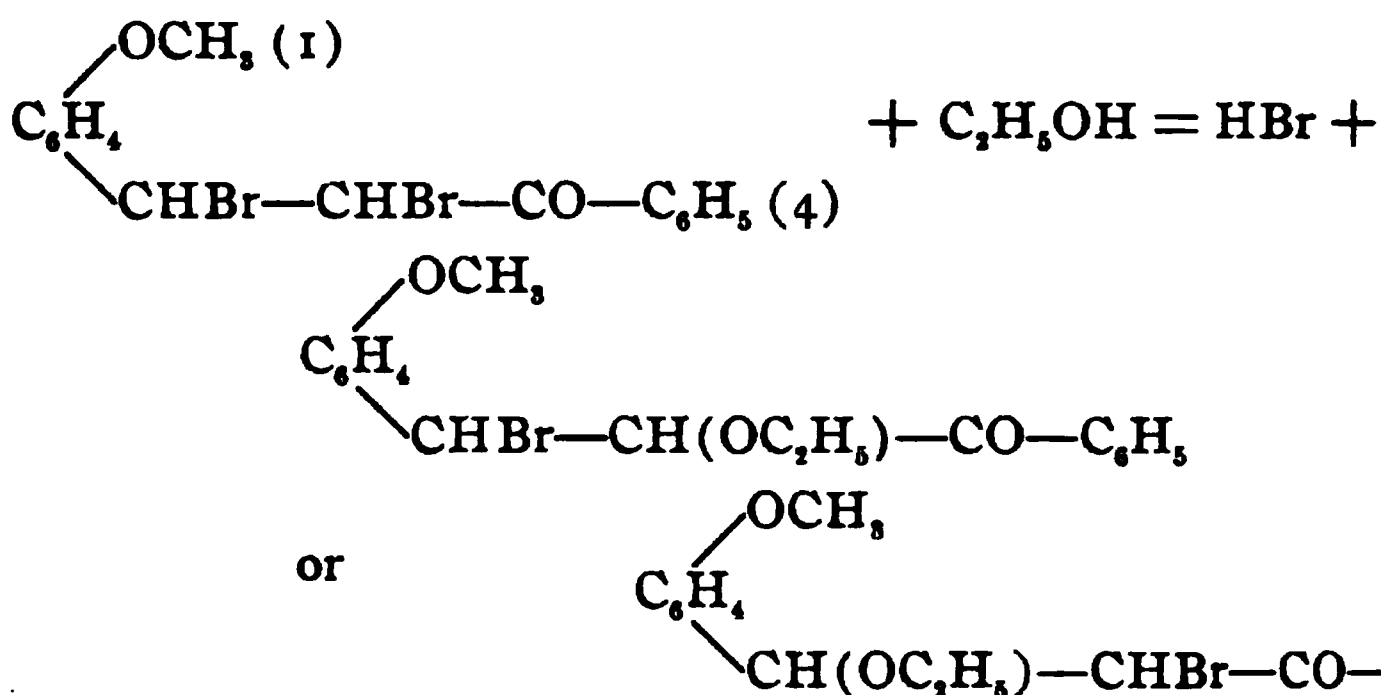
<sup>2</sup> L. Claisen: *Ibid.*, 281, 344.

tate. It decolorizes immediately a solution of potassium permanganate in the cold, but it does not yield an additive product with bromine. It is indifferent towards acetic anhydride and benzoyl chloride.

The experimental part of our work is preceded by the following brief review of the contents of this paper.

The method of preparation of anisylidene acetophenone, the starting-point of our investigation, is slightly modified, by means of which a larger yield of the compound, melting at  $78^{\circ}$ , is obtained. This substance unites readily with two atoms of bromine, forming an additive product. The dibromide can not be recrystallized unchanged from alcohol, but it separates without change from acetic ether in large crystals, melting at  $139^{\circ}$  to  $140^{\circ}$ .

When anisylidene acetophenone dibromide is dissolved in alcohol and the solution is boiled for a short time, hydrogen bromide is eliminated and an alcohol addition-product of monobromoanisylidene acetophenone is produced :

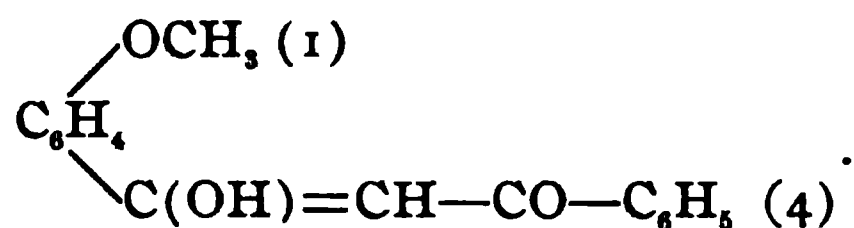


This is a saturated compound, which melts at  $73.5^{\circ}$  to  $74.5^{\circ}$ . When heated carefully in a distilling flask, no change is to be noted until the temperature reaches about  $155^{\circ}$  to  $160^{\circ}$ ; a clear liquid then comes over having the odor and boiling-point of ethyl alcohol, and yielding the iodoform reaction. If the distillation be interrupted as soon as alcohol ceases to be given off, the liquid remaining in the flask solidifies and crystallizes from alcohol or ethyl acetate in large plates, melting at  $94.5^{\circ}$ ; these are shown to be monobromoanisylidene acetophenone.

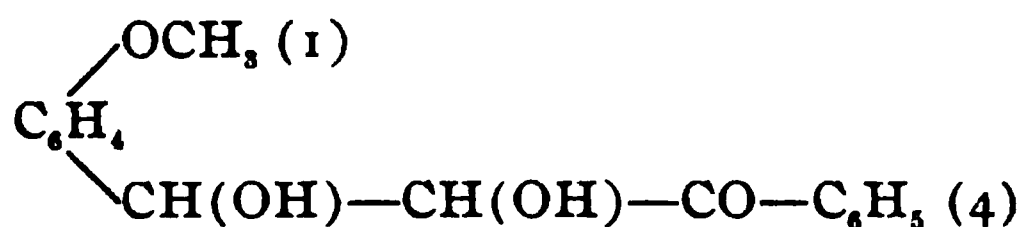
The analogous methyl alcohol addition-product was prepared,

and crystallized from methyl alcohol in fine crystals, which melt at  $102^{\circ}$ . The propyl alcohol addition-product is an oil, and is not further examined.

In a previous paper<sup>1</sup> it was shown that when anisylidene acetophenone dibromide was heated with two molecules of sodium methylate or ethylate and the resultant product hydrolyzed with hydrochloric acid, a compound was formed which melted at  $131^{\circ}$  to  $132^{\circ}$ ; this compound was called anisoyl benzoyl methane. Further investigation has shown that it consists of  $\alpha$ -oxyanisylidene acetophenone, *i. e.*, it is the  $\alpha$ - or acid-modification of the diketone,  $C_{16}H_{14}O_3$ , and is to be represented by the formula,

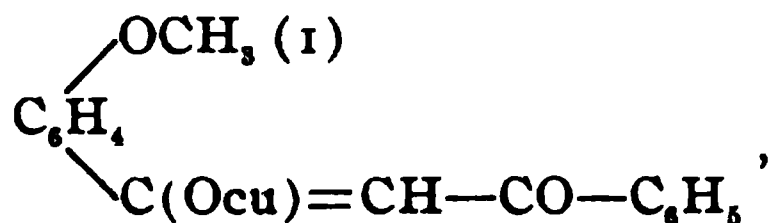


The filtrate obtained in the preparation of this compound yields an exceedingly small quantity of a silky, crystalline substance, which melts at  $90^{\circ}$  and is exceptionally soluble in alcohol; the analysis of this compound indicates that it has the composition represented by the formula,  $C_{16}H_{16}O_4$ . It may possibly prove to be the keto-glycol,



Until a method of preparation is found by which a suitable quantity of this substance can be obtained and further experimental evidence is secured, we do not care to commit ourselves regarding its structure. Should further investigation prove it to be the keto-glycol suggested above, its study will lead to very interesting results.

$\alpha$ -Oxyanisylidene acetophenone yields quantitatively a copper salt,<sup>2</sup>



which melts with decomposition at  $247^{\circ}$  to  $249^{\circ}$ .  $\alpha$ -Oxyanisyl-

<sup>1</sup> *Loc. cit.*

<sup>2</sup> cu =  $\frac{1}{2}$  atom Cu.

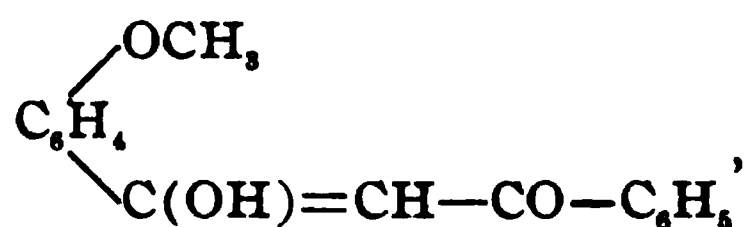
dene acetophenone is easily regenerated in a pure condition by warming this copper salt with dilute hydrochloric acid.

The action of hydroxylamine hydrochloride upon an alcoholic solution of  $\alpha$ -oxyanisylidene acetophenone gives  $\alpha,\gamma$ -methoxyphenyl-phenyl-isoxazole, melting at  $120^\circ$ ; it crystallizes from alcohol in small flakes, which possess a brilliant mother-of-pearl luster. Claisen<sup>1</sup> has shown that monoximes of the  $\beta$ - or 1,3-diketones are not generally known. In attempts to prepare them, water usually splits off and an intramolecular anhydride formation takes place, giving the isoxazoles. J. Wislicenus<sup>2</sup> succeeded in preparing a monoxime from  $\alpha$ -benzylidene acetophenone by the action of free hydroxylamine; but it showed a great tendency to lose water with the formation of  $\alpha,\gamma$ -diphenyl-isoxazole.

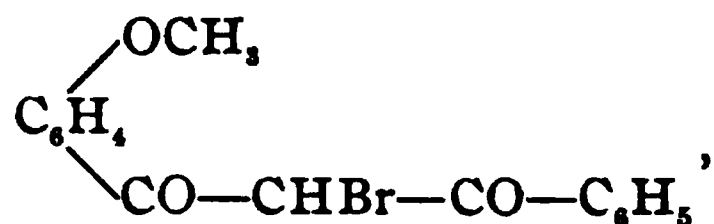
An isomeric methoxyphenyl-phenyl-isoxazole is formed by the action of an excess of potassium hydroxide upon the mixed alcoholic solutions of anisylidene acetophenone dibromide and hydroxylamine hydrochloride. It crystallizes from alcohol in small, silky needles, which melt at  $128^\circ$ .

Acetic anhydride and benzoyl chloride do not react with the hydroxyl group of  $\alpha$ -oxyanisylidene acetophenone.

Bromine seems to convert  $\alpha$ -oxyanisylidene acetophenone into a bromine derivative of the  $\beta$ -modification of the diketone. Instead of absorbing two atoms of bromine and yielding an additive product as would naturally be anticipated by the formula,



an atom of bromine is substituted for one hydrogen atom, and the compound,



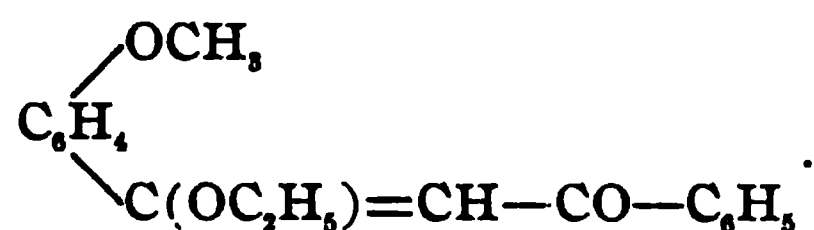
anisoyl benzoyl monobromomethane, is formed. It crystallizes well, and melts at  $127.5^\circ$  to  $128.5^\circ$ . It gives no coloration with ferric chloride and alcohol, and does not form a copper salt by

<sup>1</sup> L. Claisen : *Ber. d. chem. Ges.*, 24, 3906; 21, 2178; 24, 390; 25, 1787.

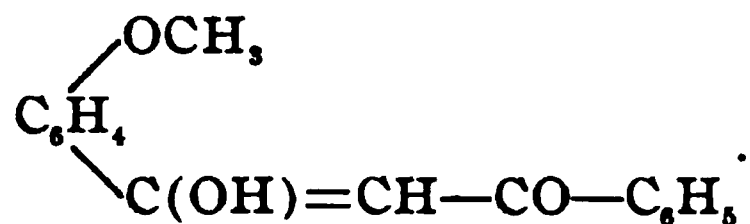
<sup>2</sup> J. Wislicenus : *Ann. Chem. (Liebig)*, 308, 250.

the addition of an alcoholic solution of copper acetate. It apparently contains no hydroxyl group.

An important part of our work is to determine, if possible, the exact course of the reaction by which the enolic-ketone is formed from anisylidene acetophenone dibromide by the action of sodium alcoholate. When one molecule of the dibromide is boiled with two molecules of sodium ethylate, the resulting product consists of an unsaturated ether,

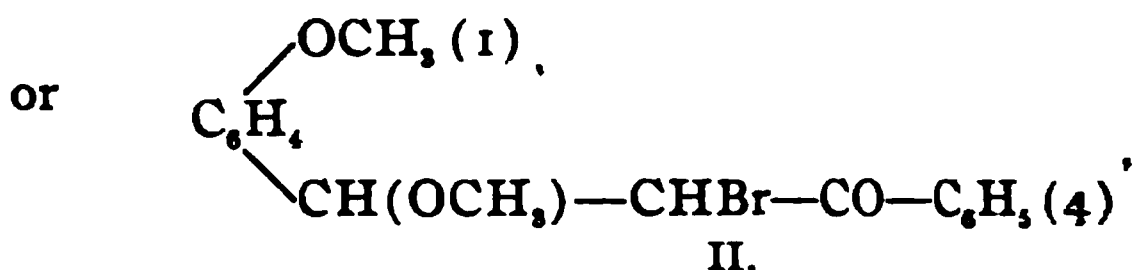
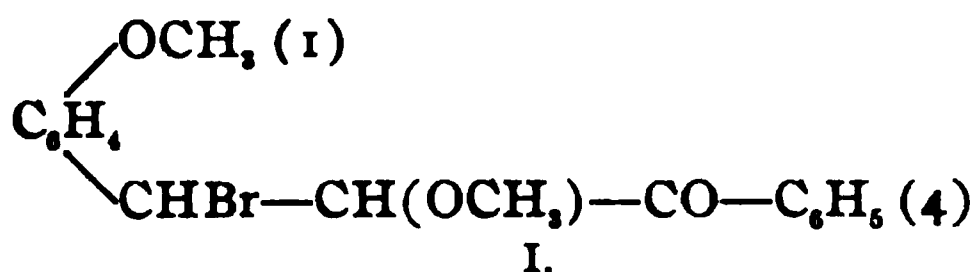


Dilute acids hydrolyze this compound with the formation of ethyl alcohol and the keto-enole,

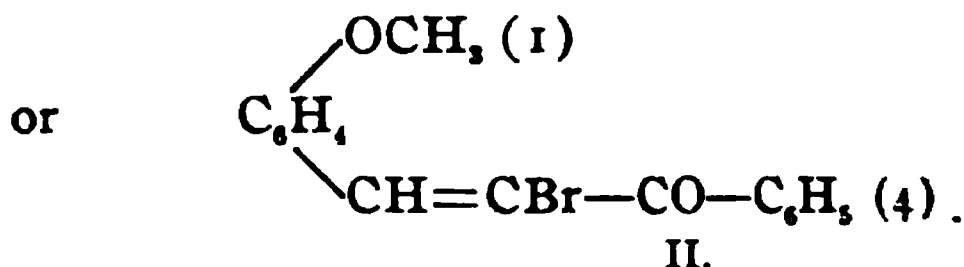
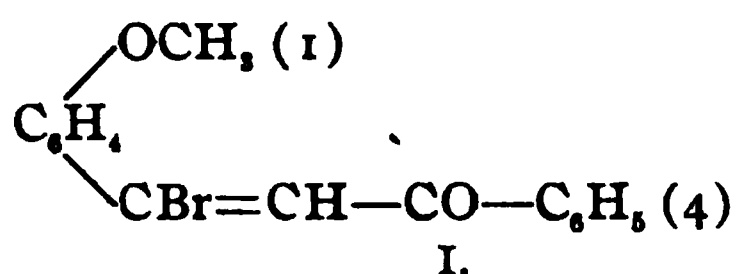


When sodium methylate is employed, the unsaturated methyl ether is produced, which also yields  $\alpha$ -oxyanisylidene acetophenone on hydrolysis. The sodium alcoholate seemed to have a double action in that it split off one bromine atom as hydrogen bromide and then replaced the second bromine atom with the methoxyl or ethoxyl group. It therefore remained to determine whether the sodium alcoholate could react under certain conditions so that the two phases of the reaction could be separated, and the intermediate products isolated.

For this purpose we treated one molecule of the dibromide with a dilute solution of one molecule of sodium methylate in methyl alcohol. The product consists of two compounds: the one crystallizing in small needles and melting at  $101.5^\circ$  to  $102.5^\circ$  is the methyl alcohol addition-product of monobromoanisylidene acetophenone, and is formed in small quantity; the other is monobromoanisylidene acetophenone, which crystallizes in beautiful plates and melts at  $94^\circ$ . On heating the methyl alcohol additive compound it loses methyl alcohol and yields monobromoanisylidene acetophenone. This alcohol addition-product should probably be represented by one of the two following structural formulas,

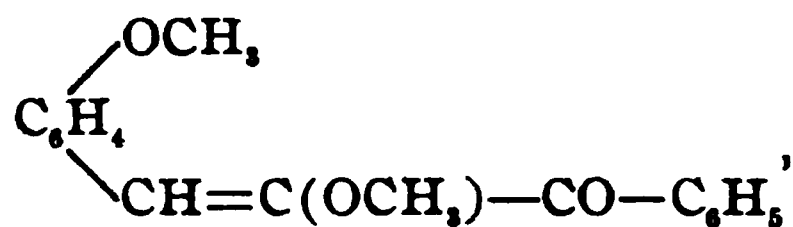


and monobromoanisylidene acetophenone by the formula,

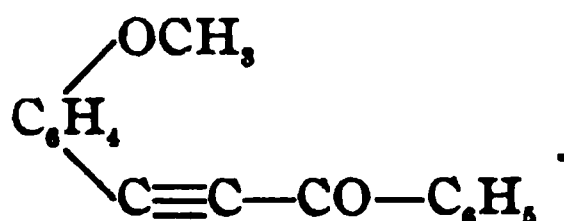


For the present we prefer the formula I for each compound for the following reasons:

If the alcohol addition-product has the structure as represented by formula II, the unsaturated monobromide resulting from it by the elimination of methyl alcohol must have the formula II, thus containing the bromine atom in the  $\beta$ -position to the methoxyphenyl group. It would be expected that by the action of another molecule of sodium methyrate upon this compound, a new ether,

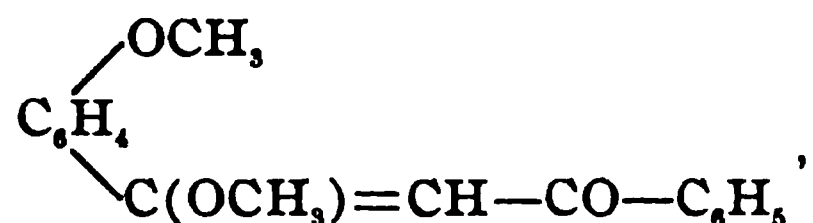


would be formed by the replacement of the bromine atom by methoxyl, or the monobromide might lose hydrogen bromide and yield a compound containing a triple linkage, benzoyl methoxyphenyl acetylene,



Neither of these compounds, however, have been obtained.

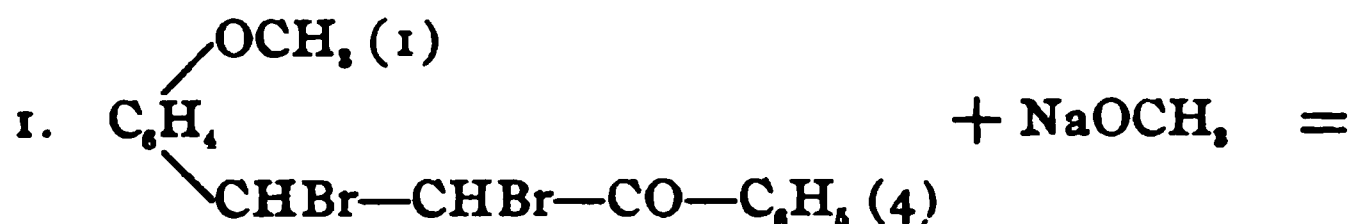
If the alcohol addition-product be represented by formula I, then by the splitting off of alcohol an unsaturated bromide having the above formula I with the bromine atom in the  $\alpha$ -position would result. Such a compound might react with one molecule of sodium methylate giving rise to the same unsaturated methyl ether,

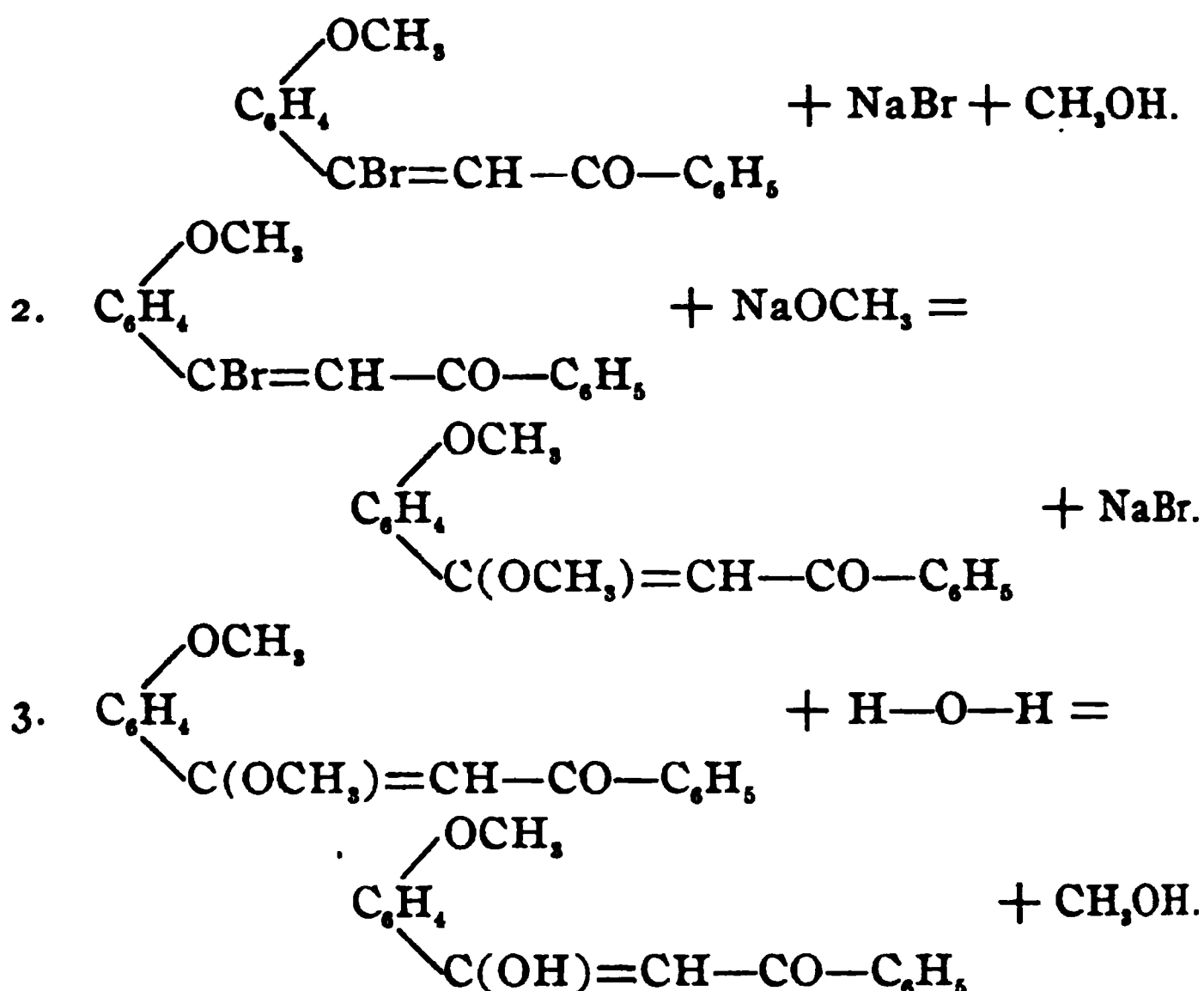


which is produced by the treatment of the dibromide with two molecules of sodium methylate, and by the hydrolysis of this ether the same keto-enole must result. Our experiments show that the reaction takes place in this manner, since the monobromide does react with sodium methylate, yielding the same ether which results by the action of an excess of methylate upon the dibromide, and from which  $\alpha$ -oxyanisylidene acetophenone is formed by hydrolysis.

The formation of  $\alpha$ -monobromoanisylidene acetophenone and of its alcohol addition-product in the same reaction would seem to indicate that one molecule of sodium alcoholate eliminates hydrogen bromide from a large part of the dibromide, yielding the unsaturated monobromide, and at the same time it replaces one atom of bromine in another smaller portion of the dibromide with the methoxyl group. It is also possible that, under the conditions of the experiment in which great care must be taken to avoid any excess over one molecule of sodium methylate, in order to prevent the elimination of both bromine atoms, that all of the sodium methylate is employed to remove hydrobromic acid, and that the small quantity of the methyl alcohol addition-product is due simply to the action of the methyl alcohol on some unchanged dibromide.

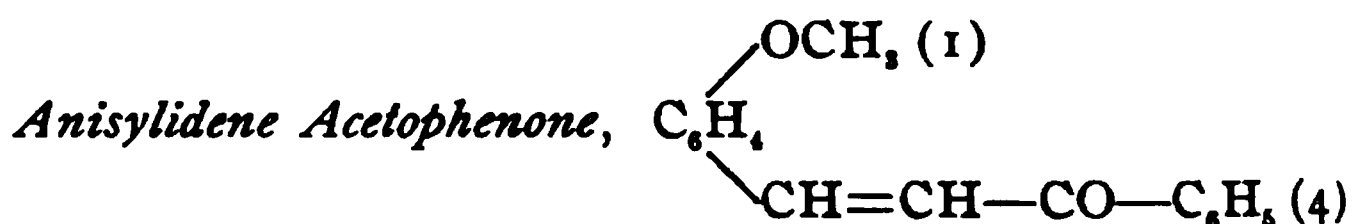
$\alpha$ -Oxyanisylidene acetophenone is probably formed by the action of sodium alcoholate upon anisylidene acetophenone dibromide in accordance with the following equations:





In the first phase of the reaction, the bromine atom in the  $\beta$ -position to the methoxyphenyl group is eliminated as hydrogen bromide with the formation of an unsaturated monobromide, while in the second stage, the bromine atom in the  $\alpha$ -position is replaced by the methoxyl group, giving an unsaturated ether, which is readily hydrolyzed into the enolic ketone.

#### EXPERIMENTAL.



This substance is very readily prepared by the following method: Twelve grams of acetophenone and 13.6 grams of anisaldehyde (molecular proportions) are dissolved in 50 cc. of alcohol and treated with 5 cc. of a 20 per cent. solution of sodium methyllate. After standing for about fifteen minutes, the solution is shaken vigorously for a few minutes, when the product separates as a yellow, crystalline solid; this is filtered by the pump, washed sparingly with cold alcohol, dried, and recrystallized from alcohol. It crystallizes from alcohol in long, light yellow

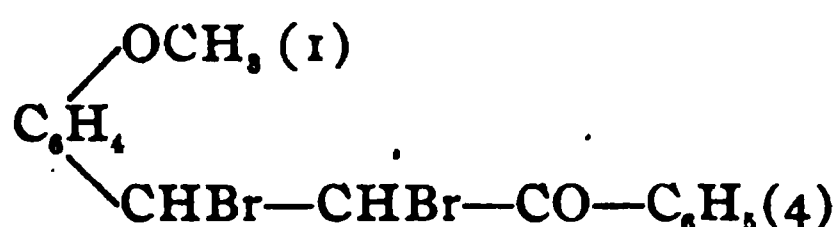


needles, and melts at  $77^{\circ}$  to  $78^{\circ}$ . It is easily soluble in hot ethyl and methyl alcohols, ether, and chloroform. Upon analysis it gave the following results :

- I. 0.1582 gram gave 0.4674 gram carbon dioxide and 0.0822 gram water.  
 II. 0.1603 gram gave 0.4733 gram carbon dioxide and 0.0846 gram water.

	Calculated for $C_{18}H_{14}O_2$ .	I.	Found.	II.
Carbon.....	80.65	80.58		80.53
Hydrogen.....	5.88	5.77		5.86

*Anisylidene Acetophenone Dibromide,*

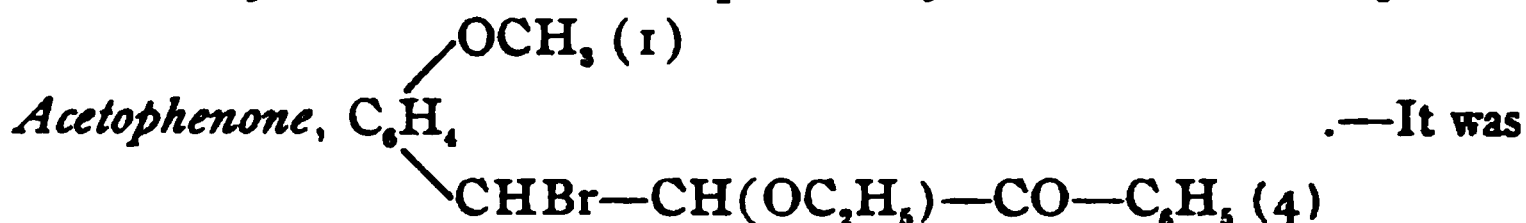


Twenty-five grams of anisylidene acetophenone were dissolved in 125 cc. of ether and the solution was cooled ; 16.8 grams (one molecule) of bromine were added slowly and with constant shaking. After two-thirds of the bromine had been introduced, the product began to separate in fine, white crystals. The crystalline precipitate was filtered, washed well with cold ether to remove any slight excess of bromine, and dried on a porous plate. It was crystallized from ethyl acetate and obtained in thick prisms, melting with decomposition at  $139^{\circ}$  to  $140^{\circ}$ . It can not be recrystallized unchanged from ethyl or methyl alcohol ; when dissolved in either of these solvents, hydrogen bromide is given off and crystalline compounds are formed, which will be subsequently described. It is readily soluble in acetic ether and crystallizes from it without evolution of hydrobromic acid ; it is only sparingly soluble in ether.

It was analyzed with the following results :

- I. 0.1807 gram gave 0.3228 gram carbon dioxide and 0.0567 gram water.  
 II. 0.1708 gram gave 0.3024 gram carbon dioxide and 0.0543 gram water.  
 III. 0.1669 gram gave 0.1566 gram silver bromide.  
 IV. 0.1825 gram gave 0.1738 gram silver bromide.

	Calculated for $C_{18}H_{14}O_2Br_2$ .	I.	II.	Found.	III.	IV.
Carbon .....	48.24	48.72	48.28		....	....
Hydrogen .....	3.52	3.49	3.53		....	....
Bromine.....	40.20	....	....	39.93		40.52

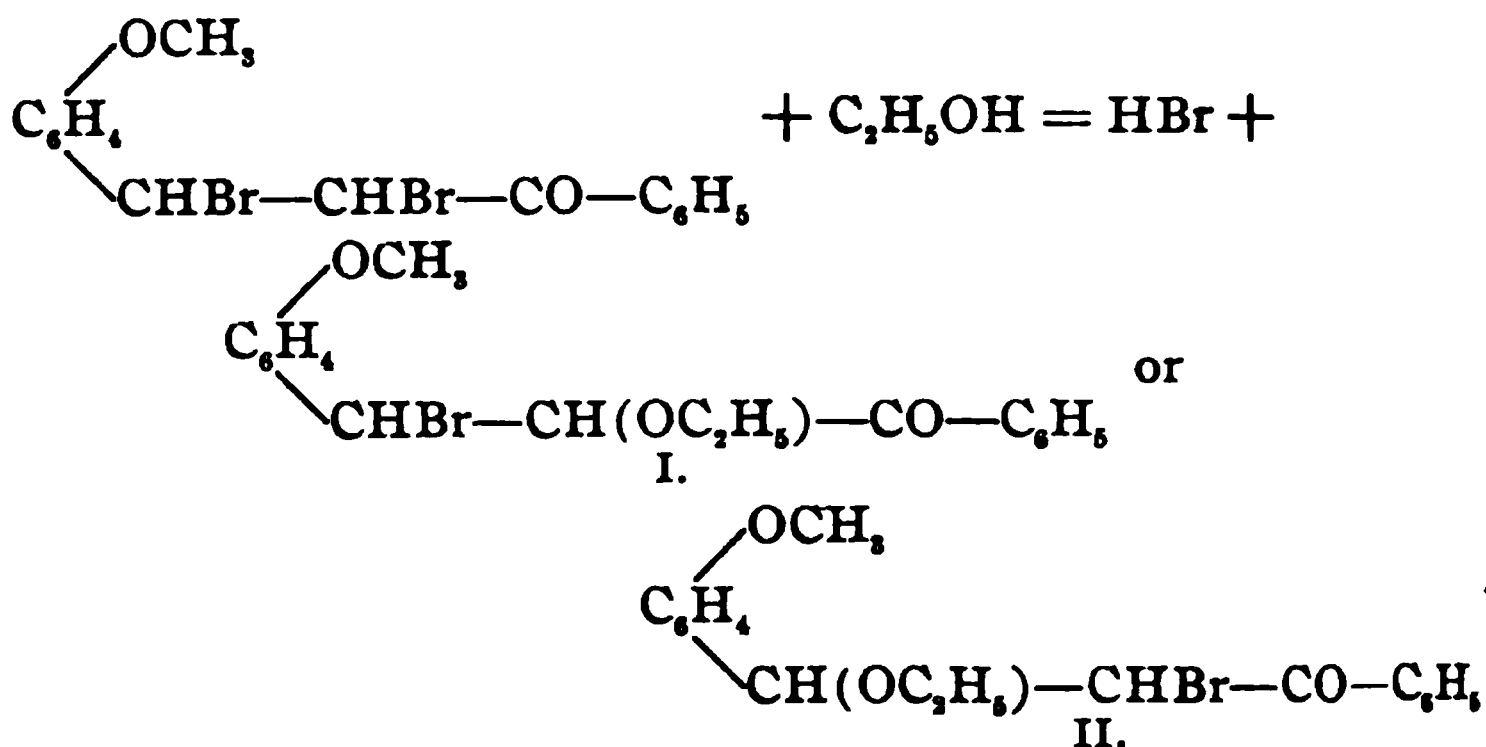
*The Ethyl Alcohol Addition-product of  $\alpha$ -Monobromoanisylidene*

noticed that when the preceding compound was crystallized from alcohol, considerable hydrogen bromide was given off and the resultant compound was quite different from the original dibromide. Fifty grams of anisylidene acetophenone dibromide were crystallized from ethyl alcohol and the resulting crystals were repeatedly recrystallized until they showed the constant melting-point,  $74^\circ$  to  $75^\circ$ . It is deposited from alcohol in long, white needles. It is unaltered by crystallization from methyl alcohol and by boiling its solution in methyl alcohol for several hours. It was dried *in vacuo*, and analyzed with the following results:

- I. 0.1832 gram gave 0.4017 gram carbon dioxide and 0.0877 gram water.  
 II. 0.1822 gram gave 0.3969 gram carbon dioxide and 0.0872 gram water.  
 III. 0.1871 gram gave 0.0970 gram silver bromide.  
 IV. 0.1671 gram gave 0.0870 gram silver bromide.

	Calculated for $\text{C}_{16}\text{H}_{15}\text{O}_2\text{Br}$	Calculated for $\text{C}_{18}\text{H}_{19}\text{O}_2\text{Br}$	I.	II.	Found. III.	IV.
Carbon.....	60.56	59.50	59.80	59.41	....	....
Hydrogen...	4.10	5.23	5.32	5.32	....	....
Bromine ....	25.23	22.04	....	....	22.06	22.15

The analysis indicated that the compound was not the monobromoanisylidene acetophenone,  $\text{C}_{16}\text{H}_{15}\text{O}_2\text{Br}$ , at first anticipated, but that it was the ethyl alcohol addition-product of this bromide. It probably results from anisylidene acetophenone dibromide according to the following equation:



For the reasons suggested in the introduction we prefer formula I.

The substance behaves like a saturated compound. When it is dissolved in carbon tetrachloride it absorbs no bromine; the first drop of bromine added gives it a permanent red color, hydrogen bromide being evolved, and when one molecular proportion of bromine is added and the solvent evaporated, a crystalline substitution-product results.

The following experiment also indicates that it is an alcohol addition-product of  $\alpha$ -monobromoanisylidene acetophenone.

Twenty-five grams of the substance (m. p.  $74^\circ$ ) were heated in a distilling flask. It melted to a clear liquid which gradually assumed a yellowish color. At about  $161^\circ$  bubbles began to form and rise from the bottom of the flask, and a clear liquid distilled over. The temperature was further increased very slowly to  $175^\circ$ , when the distillation was interrupted. Two and one-half grams of liquid distillate were obtained having the odor of ethyl alcohol, and boiling at  $77^\circ$  to  $78^\circ$ ; it yielded iodoform on treatment with iodine and potassium hydroxide, and was thus identified as alcohol. The yellow oil remaining in the flask was poured into a beaker, when it solidified at once, and was recrystallized from acetic ether; it separated in large plates, melting at  $94.5^\circ$ , and was proved to be  $\alpha$ -bromoanisylidene acetophenone.

The same addition-product results on boiling the dibromide with alcohol in a reflux apparatus for several hours. Thus, 25 grams of anisylidene acetophenone dibromide were boiled with 200 cc. of alcohol on the water-bath for several hours, and the contents then allowed to crystallize. On recrystallization from alcohol, the product separated in long, white needles, which melted at  $73.5^\circ$  to  $74.5^\circ$ , and gave the following on analysis:

- I. 0.1963 gram gave 0.1004 gram silver bromide.
- II. 0.1230 gram gave 0.1187 gram silver bromide.

	Calculated for $C_{18}H_{19}O_3Br$ .	Found.	
		I.	II.
Bromine .....	22.04	21.76	21.95

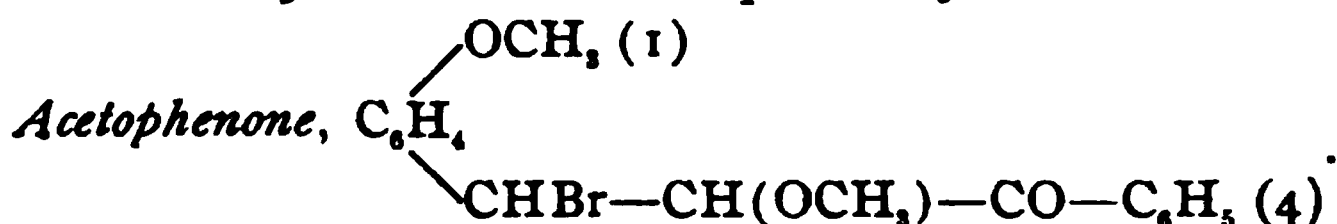
An attempt to prepare monobromoanisylidene acetophenone by boiling an alcoholic solution of the dibromide with a molecular proportion of potassium acetate resulted in the formation of

the alcohol addition-product. Twenty-five grams of anisylidene acetophenone dibromide were dissolved in 200 cc. of alcohol and treated with an alcoholic solution of 6.2 grams of potassium acetate; after boiling for three hours, the resulting potassium bromide was filtered off at once. On cooling, a compound separated from the clear filtrate in long, white needles; these were recrystallized from alcohol, and melted at  $73.5^{\circ}$  to  $74.5^{\circ}$ . Analysis showed it to be the ethyl alcohol addition-product:

- I. 0.2055 gram gave 0.1076 gram silver bromide.  
 II. 0.2008 gram gave 0.1044 gram silver bromide.

	Calculated for $C_{18}H_{19}O_3Br$ .	I.	Found.	II.
Bromine .....	22.04	22.23		22.12

*The Methyl Alcohol Addition-product of  $\alpha$ -Monobromoanisylidene*



It was to be expected that a compound analogous to the preceding one would result on crystallizing the dibromide from methyl alcohol. Accordingly, 20 grams of anisylidene acetophenone dibromide were dissolved in hot methyl alcohol, the solution boiled for a few minutes and then allowed to crystallize. Hydrobromic acid fumes were given off during the boiling of the solution and continuously during the cooling. The resulting crystalline compound was repeatedly crystallized from methyl alcohol and obtained in the form of small, white needles, melting sharply at  $102^{\circ}$ . The compound is fairly soluble in methyl alcohol, and very soluble in acetic ether; it is also readily soluble in ethyl alcohol, and crystallizes from it, without change, in small needles, melting at  $102^{\circ}$ .

Analyses of the product recrystallized from methyl alcohol and dried *in vacuo* gave the following:

- I. 0.1819 gram gave 0.3905 gram carbon dioxide and 0.0800 gram water.  
 II. 0.1818 gram gave 0.3887 gram carbon dioxide and 0.0800 gram water.  
 III. 0.2022 gram gave 0.1073 gram silver bromide.  
 IV. 0.1961 gram gave 0.1048 gram silver bromide.

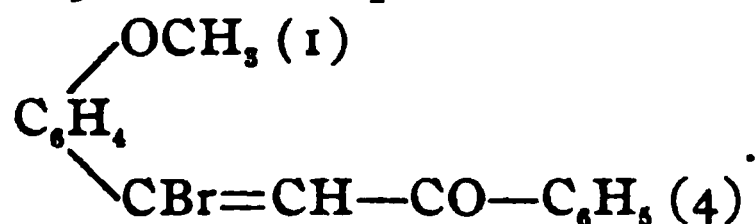
	Calculated for $C_{17}H_{17}O_3Br$ .	I.	II.	Found.	III.	IV.
Carbon .....	58.45	58.55	58.31		....	....
Hydrogen .....	4.87	4.89	4.89		....	....
Bromine .....	22.92	....	....	22.58		22.74

This compound is the methyl alcohol addition-product expected. In attempting to distil it under diminished pressure, it suffered complete decomposition. When 25 grams were heated at the ordinary pressure, the substance melted to a clear liquid and, on raising the temperature to  $160^{\circ}$ , bubbles began to rise; from  $167^{\circ}$  to  $180^{\circ}$  a small quantity of a clear distillate was obtained, while the liquid in the flask had assumed a yellowish color. At  $180^{\circ}$  the heat was removed, and, on cooling, the contents of the flask solidified at once; this solid was crystallized from ethyl acetate and obtained in large, slightly yellow-colored plates, melting at  $94^{\circ}$ , thus showing it to be  $\alpha$ -monobromoanisylidene acetophenone.

Anisylidene acetophenone dibromide dissolves in propyl alcohol with evolution of hydrogen bromide; on evaporation of the solvent, a colorless oil results, but it was not examined.

THE ACTION OF ONE MOLECULE OF SODIUM METHYLATE UPON  
ANISYLIDENE ACETOPHENONE DIBROMIDE.

*$\alpha$ -Monobromoanisylidene Acetophenone,*



To a solution of sodium methylate, made by dissolving 1.5 grams of sodium in 125 cc. of methyl alcohol, was added 25 grams of the dibromide. The dibromide dissolved at once, forming a light yellow colored solution. After boiling for one hour, a small quantity of sodium bromide had separated and the solution was no longer alkaline to litmus. The sodium bromide was separated by filtration and the filtrate allowed to evaporate slowly. A product began to separate in large, yellow plates, and, after standing for some time, it was removed and the mother-liquor allowed to evaporate to dryness, when a second product, more soluble in alcohol than the plates, was obtained. The yellow plates were washed with water, pressed on a porous plate, and crystallized from acetic ether. The resulting crystals were again rubbed on a plate to remove oily impurities, and recrystallized first from alcohol and then acetic ether. The pure product separates from acetic ether in large, beautiful plates, which

are nearly colorless and melt at  $94.5^{\circ}$ . Its composition is shown by the analysis :

- I. 0.1816 gram gave 0.4001 gram carbon dioxide and 0.0676 gram water.
- II. 0.1873 gram gave 0.4125 gram carbon dioxide and 0.0680 gram water.
- III. 0.1938 gram gave 0.1161 gram silver bromide.
- IV. 0.1898 gram gave 0.1130 gram silver bromide.

	Calculated for $C_{16}H_{19}O_2Br$ .	I.	II.	Found. III.	IV.
Carbon .....	60.56	60.09	60.06	....	....
Hydrogen .....	4.10	4.13	4.03	....	....
Bromine.....	25.23	....	....	25.49	25.33

This compound is, therefore, monobromoanisylidene acetophenone, and apparently constitutes the chief product of this reaction.

The second product, which is obtained by the evaporation to dryness of the methyl alcoholic filtrate as above mentioned, was pressed on a plate, since it contained some oil. It was then dissolved in acetic ether; plates of monobromoanisylidene acetophenone separated at first, and when the ether had nearly all evaporated, the second product was deposited in fine, white needles. A complete separation of the two compounds was made by fractional crystallization from acetic ether and then alcohol. The second product was purified by crystallization from alcohol, from which it was deposited in small, white needles, melting at  $101.5^{\circ}$  to  $102.5^{\circ}$ .

Analysis gave the following :

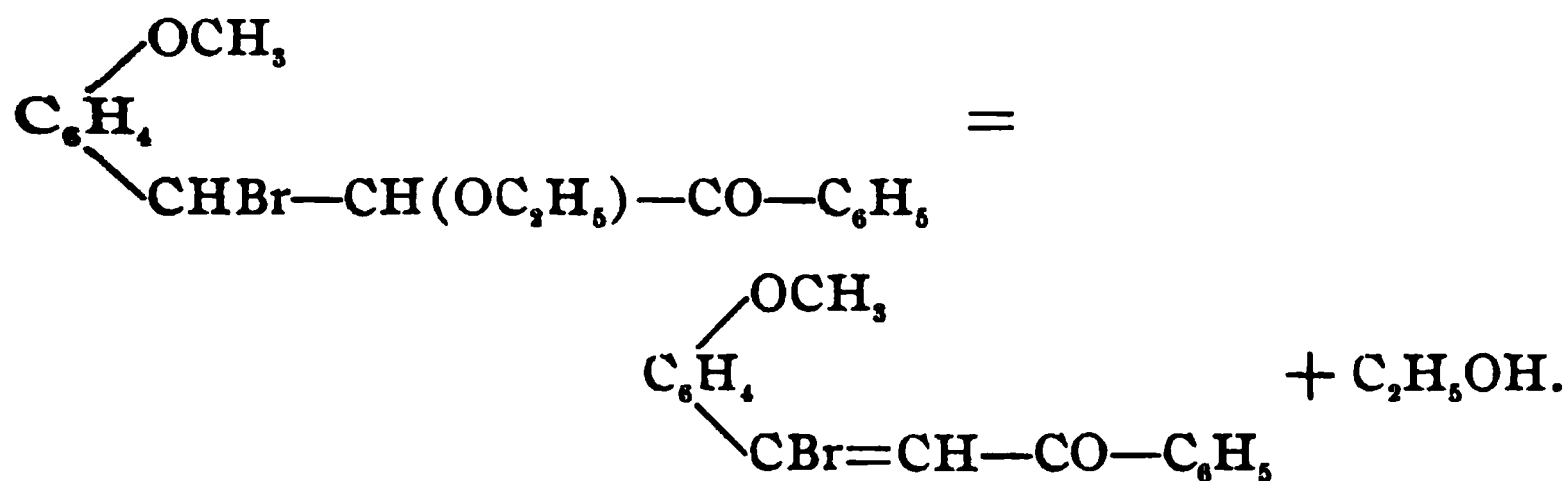
- I. 0.1805 gram gave 0.3859 gram carbon dioxide and 0.0800 gram water.
- II. 0.1808 gram gave 0.3874 gram carbon dioxide and 0.0825 gram water.
- III. 0.2096 gram gave 0.1114 gram silver bromide.
- IV. 0.2068 gram gave 0.1110 gram silver bromide.

	Calculated for $C_{17}H_{17}O_2Br$ .	I.	II.	Found. III.	IV.
Carbon .....	58.45	58.31	58.44	....	....
Hydrogen .....	4.87	4.92	5.07	....	....
Bromine.....	22.92	....	....	22.62	22.84

This substance is, therefore, the methyl alcohol addition-product of  $\alpha$ -monobromoanisylidene acetophenone.

The  $\alpha$ -monobromide is also readily formed by the action of one molecule of sodium ethylate on the dibromide. It is, however, best prepared by carefully heating the ethyl or methyl al-

cohol addition-products until the alcohol is removed, as was mentioned in the consideration of these compounds. It is purified by crystallizing from alcohol and then ethyl acetate, and forms large, well-defined plates, which melt at  $94^{\circ}$ . Its formation by the decomposition of the alcohol addition-products on heating may be represented as follows :



THE ACTION OF TWO MOLECULES OF SODIUM METHYLATE UPON ANISYLIDENE ACETOPHENONE DIBROMIDE.

Fifty grams of the dibromide were added to a solution of sodium methylate, made by the action of 7.5 grams of metallic sodium on 150 cc. of methyl alcohol. After heating the mixture for a short time on the water-bath, a reaction took place, the liquid became dark colored, and sodium bromide was deposited ; the mixture was boiled for about one hour. On completion of the reaction, the sodium bromide was dissolved by adding 200 cc. of water, a dark colored oil, heavier than water, being thrown out. Twenty cc. of concentrated hydrochloric acid<sup>1</sup> were introduced, rendering the liquid acid and changing its color from brown to light yellow ; it was then boiled for one-half hour, or until the oil was completely converted into a light yellow solid. After cooling, this was filtered off and the filtrate allowed to stand for several days, when another compound separated in very fine, white needles ; this will be described in a subsequent part of this paper. The solid was washed well with water, dried, and crystallized from alcohol, in which it is spar-

<sup>1</sup> In other experiments it was determined that dilute sulphuric acid and even acetic acid also affect the conversion of the oil into the solid, giving identically the same product as concentrated hydrochloric acid. Carbon dioxide, however, does not affect this transformation.

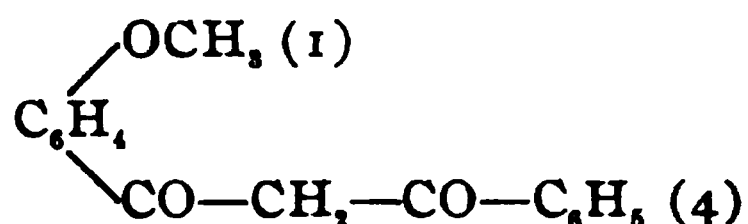
ingly soluble; it separated in fine, white crystals, melting at 130° to 131°.

The analysis gave the following:

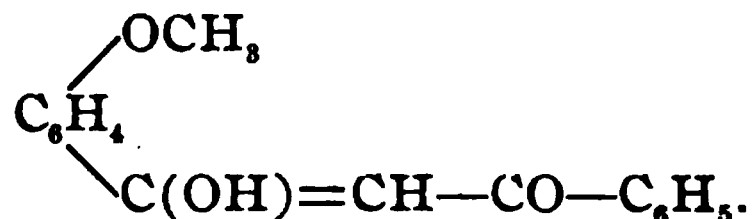
- I. 0.2003 gram gave 0.5498 gram carbon dioxide and 0.1018 gram water.  
 II. 0.1981 gram gave 0.5424 gram carbon dioxide and 0.1001 gram water.

	Calculated for $C_{16}H_{14}O_2$	Found.	
		I.	II.
Carbon.....	75.59	74.86	74.67
Hydrogen.....	5.51	5.65	5.61

This compound was first obtained by G. M. Norman and was previously described<sup>1</sup> as the 1,3-diketone, anisoyl benzoyl methane,



Its alcoholic solution is colored a deep violet-red with ferric chloride, and it is soluble in the hydroxides of potassium and sodium. Closer investigation, however, leads us to believe that this compound consists wholly, or at least for the most part, of the unsaturated ketone alcohol,  $\alpha$ -oxyanisylidene acetophenone,

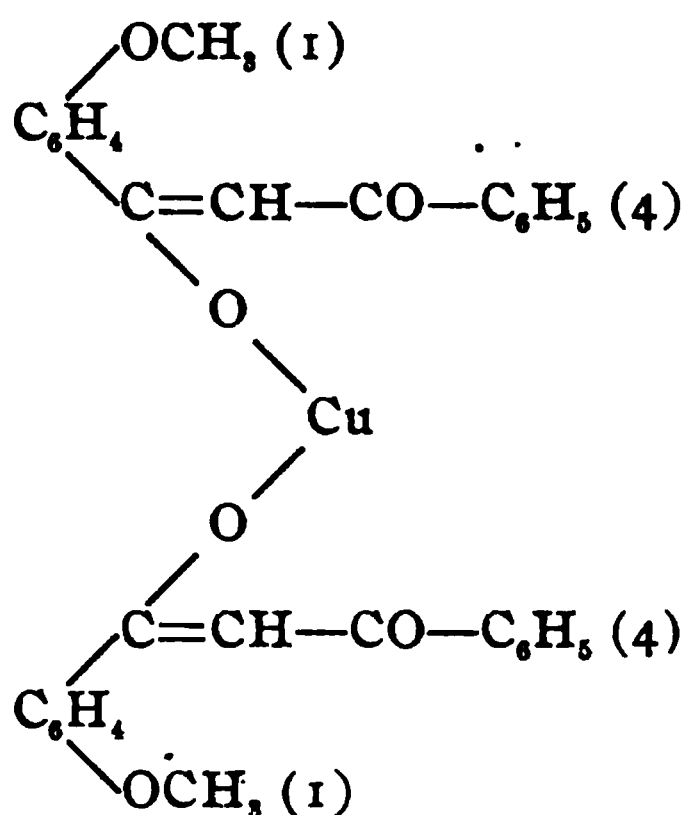


J. Wislicenus<sup>2</sup> obtained a mixture of  $\alpha$ -oxybenzylidene acetophenone and dibenzoyl methane by the treatment of benzylidene acetophenone dibromide with an alcoholic solution of potassium hydroxide, and he found that the two substances could be readily and completely separated by the action of an alcoholic solution of copper acetate; the keto-enolic modification gave an insoluble copper salt, while the other remained unchanged in the alcoholic solution. This method of treatment with alcoholic copper acetate was applied to the above-mentioned substance (m. p. 130° to 131°) with the result that it was completely converted into a copper salt.

<sup>1</sup> Pond, Maxwell, and Norman: *This Journal*, 21, 966.

<sup>2</sup> J. Wislicenus: *Ann. Chem. (Liebig)*, 308, 241.



*Copper Salt of  $\alpha$ -Oxyanisylidene Acetophenone,*

The substance is formed when an alcoholic solution of the preceding compound is treated with alcoholic copper acetate. An alcoholic solution of 3 grams of copper acetate is added slowly and with vigorous agitation to the hot, alcoholic solution of 5 grams of the above compound (m. p.  $130^\circ$  to  $131^\circ$ ). A fine, green precipitate of the copper salt separates almost immediately. The liquid above the precipitate remains colorless or slightly yellow until an excess of copper acetate is added, when it becomes green. It is essential that the liquid be kept near the boiling-point during the operation, otherwise the original compound separates. The precipitate is filtered and washed with alcohol until no trace of copper acetate is observed; it is further washed with water, then alcohol, and finally ether. It is insoluble in water, alcohol, ether, and carbon disulphide; very sparingly soluble in chloroform and benzene, and separates from the latter solvent in exceedingly small needles.

When the precipitated substance is purified by repeated washing with water, alcohol, and ether, it melts with decomposition at  $247^\circ$  to  $249^\circ$ . The analysis of such a preparation yielded the following figures:

I. 0.1984 gram gave 0.4868 gram carbon dioxide, 0.0832 gram water, and 0.0282 gram copper oxide.

II. 0.2386 gram gave 0.5850 gram carbon dioxide, 0.0955 gram water, and 0.0334 gram copper oxide.

III. 0.1825 gram gave 0.0257 gram copper oxide.

	Calculated for $C_{22}H_{20}O_6Cu$ .	I.	Found. II.	III.
Carbon .....	67.41	66.92	66.86	....
Hydrogen .....	4.56	4.66	4.45	....
Copper .....	11.16	11.36	11.18	11.25

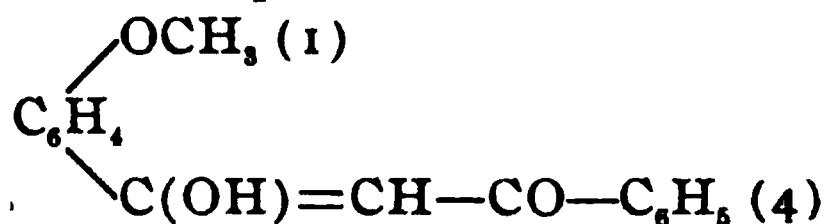
The formation of this copper salt is, therefore, represented by the following equation:



It consists of small, light green needles. It burns with a very smoky flame, leaving a residue of cupric oxide. Hot, dilute sulphuric acid decomposes it only very slowly, while hot, dilute hydrochloric acid readily converts it into cupric chloride and  $\alpha$ -oxyanisylidene acetophenone; this reaction forms an excellent method of obtaining the latter compound in a pure condition.

The alcohol was distilled off from the combined green filtrate of the copper salt and the wash alcohol, and the residue extracted with ether. The excess of copper acetate was filtered, the ethereal solution dried, and the ether evaporated in a vacuum over calcium chloride. The residue consisted of a small amount of a dark, thick oil, which did not solidify after standing for two months, and decomposed on distillation under diminished pressure. No definite compound could be obtained from it.

*$\alpha$ -Oxyanisylidene Acetophenone,*



This compound was easily regenerated by boiling the copper salt for a short time with hydrochloric acid (1 : 3), and crystallizing the product from alcohol. It separates in small, yellowish white needles, melting at  $130^\circ$  to  $131^\circ$ , and boils at  $284^\circ$  to  $286^\circ$  under 44 mm. pressure, the distillate solidifying at once to an almost white, crystalline mass. The substance, purified by distillation and subsequent crystallization from alcohol, gave the following results on analysis:

- I. 0.3009 gram gave 0.8309 gram carbon dioxide and 0.1501 gram water.  
II. 0.2516 gram gave 0.6959 gram carbon dioxide and 0.1268 gram water.

	Calculated for $C_{16}H_{14}O_3$ .	I.	Found. II.
Carbon .....	75.59	75.31	75.43
Hydrogen .....	5.51	5.54	5.60

It decomposes on distillation under atmospheric pressure. It is almost insoluble in cold alcohol, soluble in hot alcohol. It is easily soluble in chloroform, benzene, ethyl acetate, and carbon disulphide. Its alcoholic solution is colored a deep violet-red by ferric chloride, while ferric acetate precipitates the neutral iron salt of the keto-enole as a brick-red, crystalline substance, insoluble in alcohol and water. It readily forms the copper salt when treated with copper acetate and alcohol. Dilute nitric acid oxidizes it, forming a mixture of acids, probably benzoic and anisic. It dissolves in sodium and potassium hydroxide solutions and is reprecipitated with acids, melting at  $129^{\circ}$  to  $130^{\circ}$ . When the solution of the alkali is fairly concentrated and hot, the compound suffers decomposition into anisic acid, melting at  $182^{\circ}$  to  $183^{\circ}$ , and a ketone having an odor similar to that of acetophenone.

*The Compound*,  $C_{16}H_{16}O_4$ .—The filtrate obtained in the preparation of the crude  $\alpha$ -oxyanisylidene acetophenone by the action of two molecules of sodium methylate upon anisylidene acetophenone dibromide was allowed to stand; after twenty-four hours, a white, silky, crystalline substance separated. After two weeks, when no further separation of crystals was observed, it was filtered, pressed carefully on a plate to remove oily impurities and repeatedly crystallized from alcohol. It is exceedingly soluble in alcohol, and it was found best in crystallizing to make a concentrated solution and then to place the dish in a freezing-mixture, when the compound is deposited in very fine, silky needles, melting at  $90^{\circ}$ . Its alcoholic solution is neither colored by ferric chloride nor precipitated by copper acetate. Its solution in benzene removes the color of a permanganate solution very slowly.

This substance is formed in an extremely small quantity. The analysis gave values required for  $C_{16}H_{16}O_4$ .

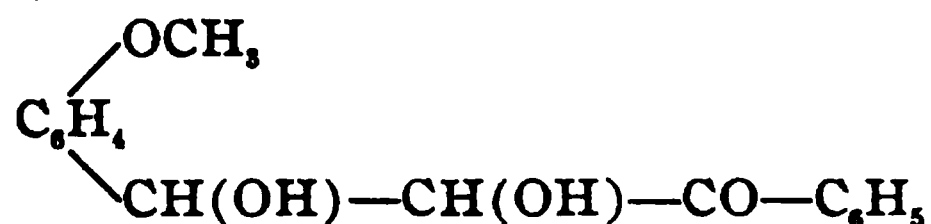
- I. 0.1573 gram gave 0.4082 gram carbon dioxide and 0.0865 gram water.  
 II. 0.1441 gram gave 0.3736 gram carbon dioxide and 0.0794 gram water.

	Calculated for $C_{16}H_{16}O_4$ .	I.	Found. II.
Carbon.....	70.59	70.77	70.70
Hydrogen.....	5.88	6.11	6.12

When one gram of the compound was boiled with an excess

of acetic anhydride for two hours, and the product poured into cold water, a thick, yellow oil separated. We were unable to isolate a definite compound from the oil.

Until a method of preparation is discovered by which a larger yield of this compound may be obtained, no satisfactory conclusions can be arrived at regarding its constitution. The analysis indicates the formula,  $C_{16}H_{16}O_4$ , and from its method of formation it is possible that the compound may prove to be the ketone glycol,



Owing to the want of material and limited time, the investigation of this substance was interrupted; the study of it will, however, be continued during the year.

#### THE ACTION OF SODIUM ETHYLATE UPON ANISYLIDENE ACETOPHENONE DIBROMIDE.

The following experiments indicate that the product of the action of two molecules of sodium ethylate or methylate on the dibromide consists of the ethyl or methyl ether of  $\alpha$ -oxyanisylidene acetophenone, which, on the addition of hydrochloric, sulphuric, or acetic acid, is converted into the corresponding alcohol and  $\alpha$ -oxyanisylidene acetophenone.

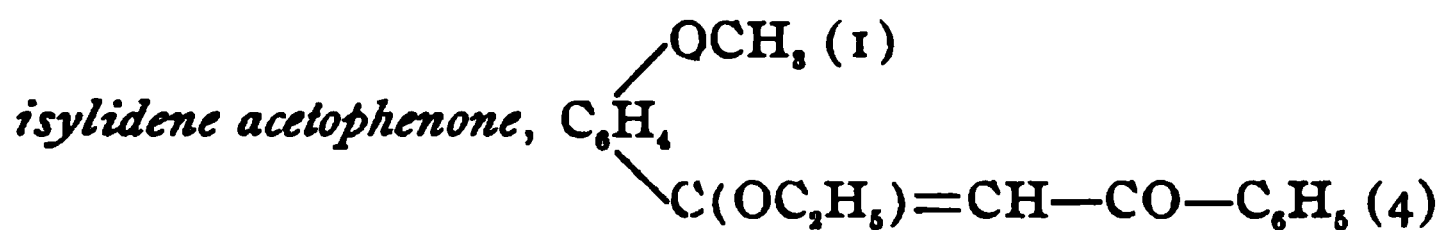
Twenty-five grams of the dibromide were added to a slight excess over two molecules of sodium ethylate (4 grams of sodium in 100 cc. of ethyl alcohol), and heated for about two hours on the water-bath. All of the alcohol was then distilled off, water was added, and the solution rendered neutral to litmus by a few drops of acetic acid; the heavy oil, which separated, was taken up with ether, the ethereal solution washed repeatedly with water, dried with anhydrous sodium sulphate, and the ether distilled off. The residue consisted of a light red colored oil.

On standing, this oil is changed, crystals being gradually deposited, and, in the course of two or three weeks, a large part of the oil is converted into a crystalline mass. This change is accelerated by the addition of acids, and, indeed, strong hydrochloric acid causes the conversion to take place in a few seconds, dilute sulphuric and acetic acids reacting more slowly. The

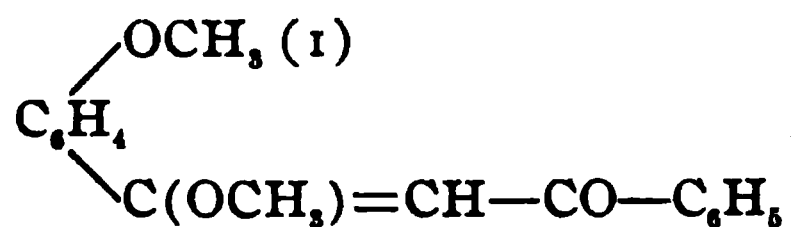
solid is identified in each case as  $\alpha$ -oxyanisylidene acetophenone.

This transformation of the oil into a solid is caused by the oil being readily hydrolyzed by the acids with the splitting off of alcohol and the formation of  $\alpha$ -oxyanisylidene acetophenone, as is shown by the following: About 15 grams of freshly prepared oil were treated in the cold with 10 cc. of dilute hydrochloric acid (1 part acid to 1 of water); the oil solidified almost immediately, with a great evolution of heat. Twenty-five cc. of water were added, the solid was filtered, and the presence of ethyl alcohol in the filtrate was easily and distinctly recognized by the iodoform test. The solid crystallized from alcohol and melted at  $128.5^\circ$ ; it gave the reaction with ferric chloride and copper acetate, and was identified as  $\alpha$ -oxyanisylidene acetophenone.

The elimination of alcohol and the production of this solid indicates, without doubt, that the substance obtained by the action of two molecules of sodium ethylate on the dibromide contains an ethoxyl group, and we regard it as the *ethyl ether of  $\alpha$ -oxyanisylidene acetophenone*,



When the dibromide is treated with 2 molecules of sodium methylate, in the same manner as above, an oil is obtained which remains unchanged for several weeks when kept in a tightly closed flask. On standing in an open flask, it is very gradually converted into a crystalline solid. When the oil is acted upon by dilute hydrochloric acid in the cold, it is quickly changed into a solid, with considerable elevation of the temperature. The solid is brittle and slightly yellow in color; it crystallizes from alcohol in small needles, melting at  $129^\circ$ , and is  $\alpha$ -oxyanisylidene acetophenone. Although the oil could not be secured in a suitable condition for the analysis, it is exceedingly probable that the substance is to be regarded as the *methyl ether of  $\alpha$ -oxyanisylidene acetophenone*,



The reaction of 2 molecules of sodium alcoholate upon anisylidene acetophenone dibromide appears to consist in first splitting off 1 molecule of hydrobromic acid with the formation of the unsaturated compound,  $\alpha$ -bromoanisylidene acetophenone, and then in replacing the bromine atom in this compound with methoxyl or ethoxyl. The resulting unsaturated ether is readily hydrolyzed by acids with the production of  $\alpha$ -oxyanisylidene acetophenone.

THE ACTION OF SODIUM METHYLATE ON THE ADDITION-PRODUCT OF  $\alpha$ -MONOBROMOANISYLLIDENE ACETOPHENONE AND ETHYL ALCOHOL.

Twenty-five grams of the addition-product were treated in the usual manner with 1 molecule of sodium methylate (2 grams of sodium in 100 cc. of methyl alcohol). On the completion of the reaction, 150 cc. of water were introduced, a dark colored oil being thrown out; hydrochloric acid was added until the liquid gave an acid reaction, and the mixture heated on the water-bath for a short time. The oil was rapidly converted into a solid, which was filtered and crystallized from alcohol; it melted at  $129^{\circ}$ , gave the color reaction with ferric chloride and alcohol, and a green precipitate with alcoholic copper acetate. It is  $\alpha$ -oxyanisylidene acetophenone.

After standing during twenty-four hours, a small quantity of the compound,  $C_{16}H_{16}O_4$ , was deposited in long, slender needles from the filtrate obtained above; it melted at  $89^{\circ}$ .

THE ACTION OF SODIUM METHYLATE ON  $\alpha$ -MONOBROMOANISYLLIDENE ACETOPHENONE.

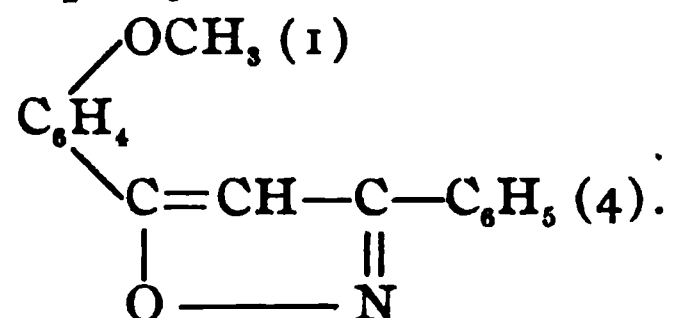
Fifteen grams of the monobromide were added to a solution of 1 molecule of methylate in methyl alcohol (1 gram of sodium in 75 cc. of methyl alcohol). After boiling for half an hour, the resultant sodium bromide was dissolved by the addition of water, the solution rendered strongly acid with acetic acid and heated for thirty minutes. On cooling, a crystalline substance separated, was filtered, and recrystallized from alcohol. It melts at  $129.5^{\circ}$ , reacts with ferric chloride and copper acetate, and is  $\alpha$ -oxyanisylidene acetophenone. The yield of the enolic ketone was very good. A small quantity of the compound,  $C_{16}H_{16}O_4$ , melting at  $89^{\circ}$ , was deposited from the filtrate.

*α-Oxyanisylidene Acetophenone and Acetic Anhydride.*—Ten grams of *α*-oxyanisylidene acetophenone were boiled with 25 grams of acetic anhydride for eight hours, and the mixture then allowed to stand for forty-eight hours. On pouring the product into ice-water, a red oil, heavier than water, was produced; this was separated, washed with water, and allowed to stand. Since it did not become solid, it was taken up in alcohol, from which a substance crystallized in yellowish white needles similar to the original compound. It melted at 130° to 131°, reacted with ferric chloride and copper acetate, and appeared to be unchanged *α*-oxyanisylidene acetophenone. The acetate could not be isolated.

No better success was attained on treatment with benzoyl chloride, as in every case the unchanged material was obtained.

ACTION OF HYDROXYLAMINE HYDROCHLORIDE UPON *α*-OXYANISYLLIDENE ACETOPHENONE.

*αγ*-Methoxyphenyl-phenyl-isoxazole,



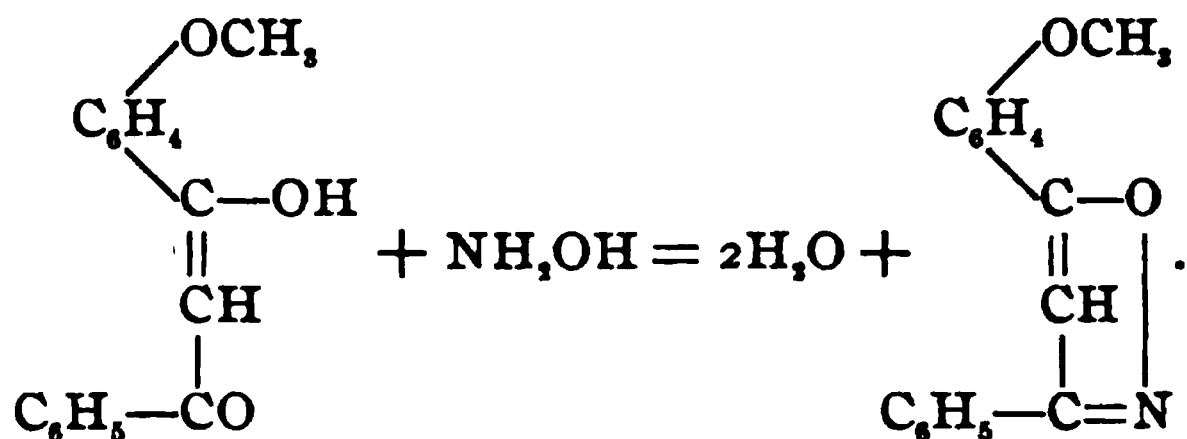
Five grams of *α*-oxyanisylidene acetophenone were dissolved in just enough hot alcohol to effect a solution in a small flask with reflux apparatus; 4 grams (3 molecules) of hydroxylamine hydrochloride were added, and the mixture was boiled gently during four hours. On cooling, a substance crystallized in beautiful, white crystals, resembling somewhat those of sulphocarbanilide. It was filtered, washed with water, dried, and crystallized from alcohol; it separated from this solvent in colorless, shining leaflets, which melted sharply at 119° to 120°. The following numbers were obtained upon analysis:

- I. 0.1502 gram gave 0.4199 gram carbon dioxide and 0.0722 gram water.
- II. 0.1935 gram gave 0.5422 gram carbon dioxide and 0.0914 gram water.
- III. 0.7050 gram gave 39.2 cc. nitrogen at 23° and 726 mm.
- IV. 0.6945 gram gave 39.4 cc. nitrogen at 24° and 726 mm.

	Calculated for $C_{16}H_{15}O_3N$ .	I.	II.	Found.	III.	IV.
Carbon .....	76.49	76.24	76.42	.....	.....	.....
Hydrogen .....	5.18	5.34	5.25	.....	.....	.....
Nitrogen .....	5.57	.....	.....	5.97	6.06	.....

This compound is insoluble in water, alkali solutions, and dilute acids, difficultly soluble in cold alcohol, more readily soluble in hot alcohol and carbon disulphide, and very easily soluble in chloroform, ether, benzene, and ethyl acetate. Ferric chloride and copper acetate do not react with its alcoholic solution. It appears to be a very stable substance. It remains unaltered by boiling with a solution of potassium hydroxide. Concentrated hydrochloric acid dissolves it very sparingly, but is without further action upon it.

It is, without doubt, an isoxazole derivative, and results from the reaction of hydroxylamine upon  $\alpha$ -oxyanisylidene acetophenone according to the equation,



It is probably analogous to the isoxazoles obtained by Claisen<sup>1</sup> by the action of hydroxylamine on the 1,3-diketones. J. Wislicenus<sup>2</sup> also obtained  $\alpha\gamma$ -diphenyl-isoxazole, melting at 140.5° to 141°, by the action of hydroxylamine hydrochloride on  $\alpha$ -oxybenzylidene acetophenone. Goldschmidt<sup>3</sup> had previously produced a diphenyl-isoxazole, melting at 141°, by the reaction of an excess of sodium hydroxide on the mixed, warm, alcoholic solutions of benzylidene acetophenone dichloride and hydroxylamine hydrochloride.

It was, therefore, of interest to determine whether the isoxazole above described or an isomeric compound would be formed by the treatment of anisylidene acetophenone dibromide with

<sup>1</sup> L. Claisen: *Ber. d. chem. Ges.*, 24, 3906.

<sup>2</sup> J. Wislicenus: *Ann. Chem. (Liebig)*, 308, 249.

<sup>3</sup> Goldschmidt: *Ber. d. chem. Ges.*, 28, 2540.



hydroxylamine hydrochloride and an excess of potassium hydroxide.

*Isomeric Methoxyphenyl-phenyl-isoxazole*,  $C_{16}H_{13}O_2N$ .—Twenty grams of anisylidene acetophenone dibromide are dissolved in 200 cc. of alcohol; to this is added a solution of 7 grams (2 molecules) of hydroxylamine hydrochloride in 10 cc. of water, and the mixture is heated to the boiling-point; 17 grams of potassium hydroxide in 20 cc. of water are then added very gradually, and with constant shaking, to the hot solution. A very vigorous reaction takes place with elimination of potassium salts, the solution assuming a yellowish red color. After standing for about ten minutes, the inorganic salts are filtered off, and on cooling the filtrate, a product separates in very fine, white needles. These are filtered, washed well with water, dried, and recrystallized from alcohol. It is deposited in very slender, silky needles, which melt at  $127^{\circ}$  to  $128^{\circ}$ .

The yield is further increased by precipitating the first alcoholic filtrate with water.

The analysis gave the following results :

- I. 0.1887 gram gave 0.5282 gram carbon dioxide and 0.0894 gram water.
- II. 0.1693 gram gave 0.4737 gram carbon dioxide and 0.0837 gram water.
- III. 0.6972 gram gave 39.2 cc. nitrogen at  $25^{\circ}$  and 728 mm.

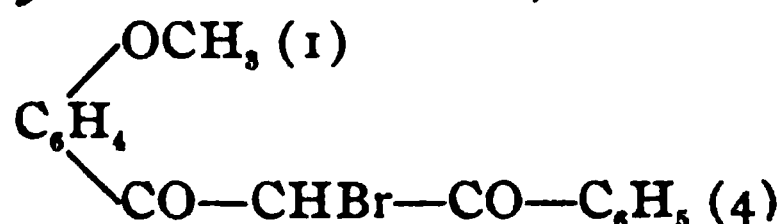
	Calculated for $C_{16}H_{13}O_2N$ .	I.	Found. II.	III.
Carbon .....	76.49	76.34	76.31	....
Hydrogen .....	5.18	5.26	5.49	....
Nitrogen .....	5.57	....	....	6.00

This compound is soluble in alcohol, ether, carbon disulphide, and readily soluble in chloroform, benzene, and acetic ether. It dissolves, to a slight extent, in hot, concentrated hydrochloric acid, and is reprecipitated on the addition of water; cold, concentrated sulphuric acid dissolves it quite easily with almost no development of color, and when the solution is poured into water, the substance is thrown out apparently unaltered. Boiling potassium hydroxide solution is without action on the substance, and ferric chloride gives no coloration with its alcoholic solution, and copper acetate no precipitate.

This compound, melting at  $127^{\circ}$  to  $128^{\circ}$ , is probably isomeric

with the preceding isoxazole, melting at 119° to 120°, although its constitution is not yet definitely determined.<sup>1</sup>

*Anisoyl Benzoyl Monobromomethane,*



When  $\alpha$ -oxyanisylidene acetophenone is dissolved in ether or chloroform and treated with one molecular proportion of bromine, hydrobromic acid is given off with gradual decoloration. On the evaporation of the solvent, a crystalline residue is obtained, which separates from alcohol in brilliant, white crystals, melting at 128°.

The analysis gave results corresponding to the formula,  $\text{C}_{16}\text{H}_{13}\text{O}_3\text{Br}$ .

- I. 0.1784 gram gave 0.3790 gram carbon dioxide and 0.0655 gram water.
- II. 0.1792 gram gave 0.3787 gram carbon dioxide and 0.0643 gram water.
- III. 0.2062 gram gave 0.1158 gram silver bromide.
- IV. 0.2060 gram gave 0.1166 gram silver bromide.

	Calculated for $\text{C}_{16}\text{H}_{13}\text{O}_3\text{Br}$ .	I.	II.	Found. III.	IV.
Carbon .....	57.66	57.94	57.64	....	....
Hydrogen .....	3.90	4.08	3.99	....	....
Bromine .....	24.02	....	....	23.89	24.08

It is soluble in alcohol, carbon disulphide, and ether; readily soluble in chloroform, benzene, and acetic ether.

Its alcoholic solution is not colored by ferric chloride, and gives no precipitate with copper acetate. It is probable, therefore, that the compound contains no hydroxyl group, and it may

<sup>1</sup> In an investigation which is being carried on in this laboratory, Mr. H. J. York has obtained the  $\alpha$ -diphenyl-isoxazole described by J. Wislicenus (*Ann. Chem. (Liebig)*, 308, 249) by the treatment of  $\alpha$ -oxybenzylidene acetophenone (resulting by the action of two molecules of sodium alcoholate upon benzylidene acetophenone dibromide and subsequent hydrolysis of the unsaturated ether with hydrochloric or acetic acid) with hydroxylamine hydrochloride. It crystallizes from hot alcohol in thick, colorless tablets, and melts at 141° to 142°. On treating benzylidene acetophenone dibromide in alcoholic solution with hydroxylamine hydrochloride and an excess of potassium hydroxide in a manner similar to the above, a compound resulted which was deposited from alcohol in thin, lustrous leaflets; these melted sharply at 140°. This compound contains nitrogen and is apparently identical with the substance described by Goldschmidt (*Ber. d. chem. Ges.*, 28, 2540) as diphenyl-isoxazole. Although at the present time it is not proved that these two isoxazoles are different, the indications are that they are isomeric and not identical, and that they are analogous to the isoxazoles obtained from  $\alpha$ -oxyanisylidene acetophenone and from anisylidene acetophenone dibromide.

be regarded as a bromine derivative of the neutral or  $\beta$ -modification of the diketone, anisoyl benzoyl methane.

We expect to continue this work in various directions, and to extend the investigations to other analogously constituted compounds.

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## A NEW VOLUMETRIC METHOD FOR THE ESTIMATION OF COPPER.

BY S. W. PARR.

Received August 13, 1900.

EXPERIMENTS looking to the use of the thiocyanates in volumetric processes have been carried on in this laboratory for over two years past. While the results obtained are in many ways very satisfactory, it is intended here to make note of one application, which gives results of great practical value.

The iodine and cyanide methods for the estimation of copper are far from satisfactory. Two methods, recently proposed in this Journal,<sup>1</sup> making use of the precipitation of copper as cuprous thiocyanate, mark a decided advance in methods. It is believed that the process here outlined has further points of advantage. It involves the precipitation of the copper as cuprous thiocyanate, the oxidation of the copper without decomposition of the alkali thiocyanate and the titration of the acidified thiocyanate with standard permanganate. In practice the two latter steps are one operation, but one filtration is necessary and for most ores thirty to forty minutes are ample for a determination from the time of weighing the sample to the time of the final titration.

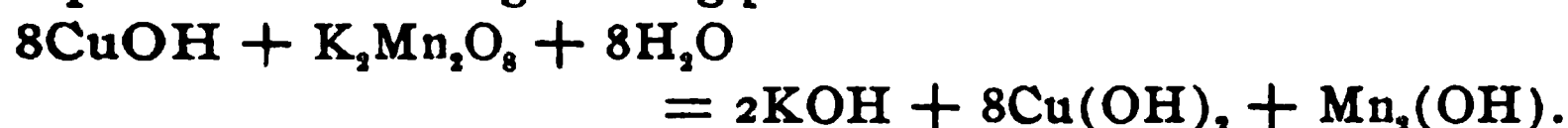
Some attention must be given to the condition of the solution before precipitating the copper as cuprous thiocyanate. If the solution contains free sulphuric acid it should not exceed 1 or 2 per cent. in amount. Stronger solutions on heating with thiocyanate have a tendency to liberate free sulphur which remains with the precipitate and in the final reading gives variable results. The same thing is true regarding hydrochloric acid. With nitric acid no free sulphur is liberated. Here, however, an excess of acid prevents the reduction and complete pre-

<sup>1</sup> This Journal, 19, 940 (1899) and 20, 610 (1900).

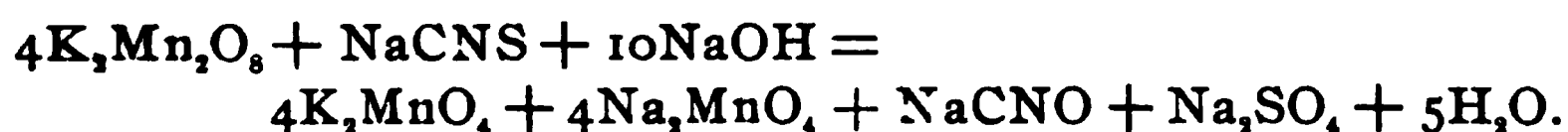
precipitation of the copper, so that in any case an amount of free acid in excess of 1 or 2 per cent. is to be avoided. Since the greatest safety seems to reside with the nitric acid it is preferred. This is an advantage also for in the initial treatment of mattes, ores, etc., it avoids the necessity of evaporating the solution to sulphuric acid fumes for the removal of the nitric acid. Further it may be noted that a small amount of sulphuric acid, resulting from the action of strong nitric acid or otherwise present, does not interfere with the precipitation. The reduction of the copper is best effected by a strong solution of sulphur dioxide, a few cc. being added from time to time. A 10 per cent. solution of sodium sulphite may be similarly used but it is better not to add acid to such a solution to liberate the sulphurous acid but allow it to be liberated by the free acid of the copper solution. The next point to be observed is the addition of the alkaline thiocyanate. The precipitated cuprous thiocyanate is very appreciably soluble in an excess of this reagent. Two cc. of a 10 per cent. solution of potassium thiocyanate will precipitate several times the amount of copper that could be conveniently handled in the subsequent titration; hence, that amount of reagent is sufficient to use, and at the same time there is no danger of re-solution of the precipitate. This reagent may be added with the reducing agent, before or after it, seemingly without preference. Heating on a water-bath or hot plate with stirring should be continued till the separation of the precipitate is complete and the supernatant liquid becomes perfectly clear. This requires from five to ten minutes.

The filtration is best made on a thick asbestos felt well packed in a  $1\frac{1}{2}$ -inch porcelain filter funnel using a pump. A felt  $\frac{1}{8}$  inch or more thick should be used. The washing which should be made with hot water is complete when the filtrate, upon acidifying, will not decolorize a drop of permanganate. Special care should be taken that none of the precipitate passes through with the filtrate. The filter with the asbestos-pulp is returned to the beaker, 2 or 3 cc. of caustic soda (10 per cent.) solution are added, well stirred and warmed to  $60^{\circ}$  or  $70^{\circ}$ . The mixture after a few minutes is ready for titrating with the standard permanganate, the object being first to add to the alkaline mixture the amount of permanganate needed to oxidize the

cuprous hydroxide formed from the addition of the alkali, then to acidify and proceed with the rest of the titration to oxidize the thiocyanic acid. The first part of the reaction, that which takes place in the alkaline condition, is confined to the copper so long as any cuprous hydroxide remains. The following equation represents the change taking place:



Now it is not necessary that at the exact end of this reaction on the copper the change should be made to the acid condition, but it is necessary that this point be fully passed in order that upon acidifying there may not be reprecipitated some cuprous thiocyanate. Fortunately it is easy to tell when this point has been passed, and in this way, when the copper has been all oxidized there begins a reaction between the alkaline thiocyanate and the permanganate which results in the formation of the green manganate thus:



It will be seen, therefore, that the bright yellow of the cuprous hydroxide becomes more and more mixed with the dark brown of the  $\text{Mn}_2(\text{OH})_6$  and soon fails to give any yellow tint whatever; further addition of permanganate produces a decided green tint to the liquid part of the mixture. If after a minute or two this remains permanent it may be known that all the copper has been oxidized.

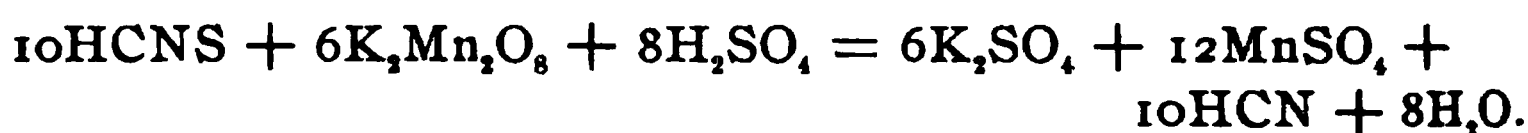
Dilute sulphuric acid (1 : 5) is now slowly added with constant stirring to prevent heating. When the solution becomes clear a decided excess of the dilute acid is added, the whole warmed to 60° or 70°, and the titration continued to the usual pink end reaction. If in this part of the reaction the brown manganic hydroxide does not quickly disappear by solvent action of the acid, it is evidence that the acid is not present in sufficient excess or that the amount started with has been largely exhausted and more acid should be added. Concentrated acid may not, at any time, be added to the solution because of the tendency to form the carbon oxysulphide.

Notwithstanding the above somewhat roundabout reactions,

the whole process proceeds uniformly as if the reaction were simply thus:  $10\text{CuCNS} + 7\text{K}_2\text{Mn}_2\text{O}_8 + 21\text{H}_2\text{SO}_4 = 7\text{K}_2\text{SO}_4 + 14\text{MnSO}_4 + 10\text{HCN} + 10\text{CuSO}_4 + 16\text{H}_2\text{O}$ . This reaction serves to emphasize two things: first, that much sulphuric acid is needed in the reaction, and second, that the amount of permanganate used is high in proportion to the copper present.

This is further evident when it comes to the matter of calculation. In determining the permanganate factor for copper from its iron standardization it is noted that by the above equation the molecular ratios are:  $10\text{Cu} : 7\text{K}_2\text{Mn}_2\text{O}_8$ . Comparing with the usual iron ratio  $1 : 10$ , we find the ratio between copper and iron to be  $10\text{Cu} : 70\text{Fe}$  or  $63.6 : 392$  or  $0.1602$ . Hence the iron value per cubic centimeter of the permanganate multiplied by the factor  $0.1602$  will give the copper value per cubic centimeter. While this feature is an advantage where the copper content is low, it also calls for the use of small quantities where the copper content is high, otherwise the consumption of permanganate will be excessive. It is therefore best to weigh out 1 gram of the substance and make up to 250 or 500 cc., and take an aliquot part as seems to be indicated by the depth of color due to the copper present. A decinormal solution of permanganate having an iron factor of  $0.0056$  would have a copper factor of  $0.000897$ ; hence, an amount of copper in excess of 40 milligrams would use more than 50 cc. of permanganate.

It may be well to note further that the amount of permanganate used in oxidizing the copper is only about one-sixth of the amount used in subsequent titration; hence, there is little danger of overrunning the total amount in the alkaline part of the process where the end reaction is indefinite. This point is further illustrated by the equation for thiocyanic acid alone, thus:



The process evidently demands that the thiocyanate precipitate be very complete, exact and free from sulphur. That these conditions are easily attainable seems to be indicated by the results. Removal of other metals is not necessary, even silver does not interfere because unaffected by the treatment with caustic alkali, and the insoluble silver thiocyanate acts so very

slowly on permanganate solution as not to vary the end-reaction appreciably. Results have been obtained as follows:

A solution of copper sulphate was made and acidified with nitric acid. Careful electrolytic determination of the copper gave a factor for each cubic centimeter of 0.00661 gram.

Solution taken. cc.	Titration. cc.	Indicated copper in mg. per cc.	Error as referred to electrolytic result in mg. per cc.
(a) 5.....	32.8	6.63	+0.02
(b) 5.....	32.6	6.59	—0.02
(c) 5.....	32.8	6.63	+0.02
(d) 5.....	32.5	6.57	—0.04
(e) 5.....	32.7	6.60	+0.01
(f) 10.....	65.6	6.63	+0.02
(g) 20.....	130.6	6.59	—0.02
(h) 40.....	372.0	6.60	—0.01

The reaction between a thiocyanate and permanganate seems to be very constant. One exception only has been found and that not necessarily of such a nature as to interfere with the accuracy of the above process.

A solution of 1.5 grams of ammonium thiocyanate to a liter of water has a strength very nearly corresponding to N/10 permanganate solution. Now up to this point of dilution the thiocyanate seems to react regularly and in accordance with the above reactions. If, however, the thiocyanate be largely diluted beyond this point, the amount of permanganate used up in the reaction is appreciably less than the same quantity of thiocyanate would use, if undiluted. For example, a measured quantity, say 10 cc., of thiocyanate, if diluted 200 times, will titrate approximately 0.1 cc. of N/10 permanganate less than the same solution would use if undiluted.

This tendency to a lower titration seems to be corrected by acidifying more strongly with acid to correspond with the dilution; also in a less degree by somewhat higher heat.

Such possibility of error, however, is easily guarded against by keeping the solution of copper and thiocyanate in a concentrated form, or rather refrain from diluting the mixture, the necessary reagents alone furnishing all needed dilution from the time of treating the asbestos pulp and precipitate with alkali to the final titration with the permanganate. I desire to acknowledge my obligation to Mr. A. R. Johnston for the analytical data connected with this work.

## FREE ARSENIOS OXIDE IN PARIS GREEN.

BY E. W. HILGARD.

Received July 6, 1900.

IN view of the many reclamations and conflicting results as to the content of free arsenious oxide in commercial Paris green that have reached this station since the publication of Bulletin No. 126, in which the unsatisfactory quality of the average material now on the market was discussed, it seems desirable to review briefly some of the causes of the discrepant results of different analysts.

The serious injury to foliage frequently resulting from the use of the commercial article led this Station to investigate specially the subject of the presence and correct determination of free  $\text{As}_2\text{O}_3$ . It should be understood that in the arid climates, where practically no rain falls during the summer, the absence of the periodic washing-off of the leaves, such as frequently recurs in the region of summer rains, permits of injury from a much smaller percentage of the free arsenical compound. The limit above which such injury occurs was found by our experience to be 4 per cent. of free arsenious oxide; and whenever that amount is exceeded we recommend the addition of a certain proportion of slaked lime to counteract its effects.

The New York law requiring the total percentage of arsenious oxide in Paris green to be "not below 50 per cent.," wholly omits any reference to the free or combined state of the compound. Hence some manufacturers have discarded all care in this respect, and greens containing as much as 20 per cent. and more, of the free oxide, are of frequent occurrence. Such articles are extremely objectionable in this climate at least, and probably elsewhere. This law certainly needs amendment, as it puts a premium on careless manufacture, or fraud. In some samples submitted to us it was evident that the "white arsenic" had been added in bulk to the green, as in the case of other adulterants, among which gypsum, Glauber's salt, chalk, and pipe-clay were easily identified by the microscope as well as by chemical tests. Microscopic examination proved, in fact, to be such a convenient and decisive test in most cases, that it is



always the first thing we do, as it frequently renders any further chemical work wholly unnecessary. The cogency of the microscopic examination is not so generally appreciated by chemists as it is by mineralogists ; but there is no excuse for any mistakes in such work, as the crystalline forms of adulterants are perfectly conclusive, either directly, or after solution and evaporation. Especially can there be no mistake about the lustrous, sharp octahedrons of arsenious oxide, whether they be scattered about among the globules of Paris green, or, as is most commonly the case, adherent to the surface of the latter ; so that in case of large proportions of the free arsenic, the globules are set with sharp octahedrons like a circular stone-saw or "diamond-drill." In most of such samples we have found the bulk of the free arsenic to be in this condition.

Such crystals dissolve very slowly in cold water, and even when  $40^{\circ}$  or  $50^{\circ}$  C. is used ; and as a high temperature disintegrates the green globules, it does not seem admissible to employ it. After twenty-four hours' treatment with indefinite quantities of cold water, the arsenical crystals were sometimes still discernible as transparent, obtuse ridges around the outside of the globules, still constituting quite one-half of the total free arsenious oxide.

It is thus obvious that by treatment of Paris green for a few hours, with such small amounts of water as we find are in use at some of the Eastern stations (100 to 300 cc. per gram of green), too low results must be obtained. As in orchard practice the proportion of water used is from 500 to 1000 times the weight of the green employed, it seems proper to conform the analytical practice to this practice, in order to obtain results that shall represent the actual facts of the case. This is what we have adopted as a rule, together with the prolonged agitation of the green with the water, which is likewise practiced in the orchard. It is from this cause, doubtless, that our results are almost uniformly above those of our Eastern colleagues ; but I think we are justified in adhering to what is manifestly in accordance with the practical outcome. It has been repeatedly said to us, in reply to our insistence on the microscopic examination, that "no Eastern chemist practices it." To this I have only to say, that in this as in numerous other cases, the microscopic examination usually affords so much more prompt and decisive informa-

tion regarding purity or adulteration than mere analysis, that I cannot but regard its omission as a serious mistake, in neglecting important evidence so readily obtainable.

It has been suggested that we do not take into account the "solubility of Paris green in water," as estimated from the amount of copper going into solution. But as in several cases we have found verdigris to pass into the first filtrates, the dissolution of copper being reduced to a mere trace when the washing was continued beyond 1000 cc. per gram, it is manifest that this correction cannot be applied safely without special precautions, even if it were certain that Paris green is soluble; in any case, the arsenic that passes into solution in this form cannot exceed a fraction of 1 per cent. In the case of a sample containing somewhat less than 4 per cent. of free arsenious oxide, for which an Eastern chemist has reported only 0.9 per cent., we found in the first 1200 cc. applied to 1 gram of substance, 0.26 per cent. of copper, for which, supposing it to represent Paris green, a similar weight of arsenious oxide would have to be deducted. But an additional 600 cc. failed to give *any* reaction for copper, even when concentrated to 25 cc., although a small amount of arsenic still continued to come. The microscope showed the cause of this continued slight contamination to be a few readily recognizable octahedrons of arsenious oxide adherent to the surface of the globules, here and there. Practically the same results were obtained by a slow percolation of cold water, when after the passage of 2000 cc. no copper reaction could be found; but a trace of arsenic continued to come through at the end of the fifth liter of water. In the sample thus washed, however, no arsenical crystals could be detected by the microscope, but only fragments of crushed globules of Paris green, whose form and aspect cannot be mistaken for arsenious oxide by any practiced eye.

It is thus obvious that extraction with a few hundred cc. of water for a few hours cannot yield a proper measure of the free arsenic present in Paris green. Not less than 600 cc., and preferably not less than 1000 cc., or 1 liter per gram, should be employed, and the extraction continued for twenty-four hours.

As to the test prescribed by at least one Eastern station, *viz.*, the solubility of the pure green in ammonia, it is utterly illusory

so far as "white arsenic" is concerned. Even if the latter were not itself rather readily soluble in ammonia, the fact stated in all books of reference that it is easily soluble in ammonium arsenite (which is of course formed when Paris green is dissolved in ammonia) fully disposes of any claim of this test to acceptance.

UNIVERSITY OF CALIFORNIA, June 30, 1900.

## A METHOD OF DETERMINING FREE ALKALI IN SOAPS.

BY R. E. DIVINE.

Received July 26, 1900.

THE usual method of making this determination prescribes a separation of caustic from carbonated alkali by drying the soap, dissolving in absolute alcohol, and after filtering and washing the undissolved carbonate with alcohol and dissolving in water to titrate the solutions containing caustic and carbonate, respectively, with standard acid. This method is open to several objections, aside from the amount of time consumed. If it is desired to obtain accurate results on the caustic and carbonate separately, the preliminary drying of the soap introduces an error since the caustic alkali will take up carbon dioxide from the air unless the drying is done out of contact with air. It is quite a troublesome process to filter an alcoholic soap solution if one is not provided with appliances to keep the funnel hot during filtration. Dudley and Pease<sup>1</sup> use an alcoholic solution of stearic acid for titrating the caustic, but still filter from undissolved carbonate, and determine the latter in the usual manner. In the following process the writer has succeeded in eliminating filtration. For this method it is necessary to provide three standard solutions:

1. Hydrochloric acid, N/10 (for standardizing 2).
2. Caustic soda, N/10, in alcohol.
3. Stearic acid, N/10, in alcohol.

2 and 3 should be exactly equivalent one to the other, titrated warm with phenolphthalein indicator.

Two grams soap (which needs no drying) is weighed into a round-bottomed flask, of about 300 cc. capacity, and 50 cc. alcohol poured upon it. N/10 stearic acid is now run in from a

<sup>1</sup> *Engineering and Railroad Journal*, (1891), 551.

burette in amount judged to be sufficient to neutralize the free alkali in 2 grams of the soap, some phenolphthalein added, and the flask then stoppered with a cork stopper, through which passes a glass tube about 30 inches long and of about  $\frac{1}{4}$  inch internal diameter, the lower end ground to a point on a grindstone, and the purpose of which is to serve as a reflux condenser. The flask and contents are placed on a steam-bath and heated thirty minutes, at the expiration of which time the solution should be quite clear and show no alkali with the phenolphthalein. If the solution turns red during the boiling, showing that an insufficient quantity of stearic acid has been added at first, add more of that solution until the color disappears, then several cubic centimeters in excess, and heat twenty minutes further. The flask is now removed from the bath and, after a few minutes' cooling, titrated with N/10 caustic soda. The difference between the number of cubic centimeters stearic acid solution added and the number of cubic centimeters caustic soda used to back titrate is equivalent to the total free alkali present.

While the first flask is heating, weigh out in a similar flask 2 grams of soap and add 50 cc. alcohol and place on the steam-bath. When the first test is finished, calculate roughly the total alkali, assuming the total quantity to be carbonate. Now add to the second flask an amount of 10 per cent. barium chloride solution sufficient to precipitate alkali found,<sup>1</sup> heat a few minutes, add phenolphthalein, and titrate with N/10 stearic acid. The titration must take place slowly and with thorough agitation of the liquid for the reason that the sodium or potassium hydroxide reacts with the barium chloride added and forms sodium chloride and barium hydroxide. The latter is not very soluble in the alcoholic liquid and sufficient time and pains must be taken to ensure its complete neutralization by the stearic acid. A blank test should be made on 50 cc. of the alcohol, since this frequently contains carbon dioxide, and the number of tenths cc. N/10 caustic soda necessary to neutralize the free acid in this quantity of alcohol added to the reading of the stearic acid burette in the second test. This corrected reading gives the number of cubic centimeters N/10 stearic acid used to neutralize the caustic alkali in 2 grams of soap. The difference between the total

<sup>1</sup> 1 cc. N/10 stearic acid = 0.0122 gram  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  or 0.122 cc. 10 per cent. barium chloride solution.

alkali found and the caustic will, of course, give the carbonate. For example : 2 grams of soap and 15 cc. N/10 stearic acid ; run in 3.2 cc. N/10 caustic soda to back titrate. Consequently,  $15 - 3.2 = 11.8$  cc. N/10 stearic acid equivalent to total free alkali.

To neutralize the caustic in the sample treated with barium chloride was required 4.1 cc. N/10 stearic acid. Fifty cc. of the alcohol used required 0.2 cc. N/10 caustic soda, then  $4.1 + 0.2$ .

4.3 cc. N/10 stearic acid to neutralize free caustic alkali.  
 $11.8 - 4.3 = 7.5$  cc N/10 stearic acid to neutralize carbonated alkali.

1 cc. N/10 stearic acid = 0.004 gram caustic soda or 0.0053 gram sodium carbonate.

The above figures calculated to percentage would be :

0.86 per cent. caustic soda and 1.99 per cent. sodium carbonate.

It is to be noted that a rubber stopper cannot be used in the flasks for dissolving the soap on account of the sulphur in the rubber, which decolorizes an alcoholic solution of phenolphthalein. The method is applicable to all soaps which do not contain fillers which react with the standard solutions employed.

BUFFALO, July 24, 1900.

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## INVESTIGATIONS ON THE DETERMINATION AND COMPOSITION OF HUMUS AND ITS NITRIFICATION.

BY CHARLES RIMBACH.

Received July 30, 1900.

THE investigation on the nitrification of the *matière noire* of Grandeau, here discussed, was undertaken on the suggestion of Prof. Hilgard, to test the question whether or not that substance is to be regarded as a source of nitrates under the influence of nitrifying bacteria as has been assumed, but never definitely proved. The method of preparation consists in treating the soil with dilute hydrochloric acid to remove the lime and magnesia with which the humus substance forms insoluble compounds ; and after washing with distilled water, until the filtrate is neutral, extracting it with 6 per cent. ammonia. On evaporation the solution leaves the *matière noire* behind.

As a medium containing the carbonates of lime and magnesia is most favorable to nitrifying bacteria, the compound of the

humus with these metals was employed for the experiment in order to simplify conditions. For this purpose the ammonia extract from a soil was precipitated with hot solutions of gypsum and magnesium sulphate ; the compound, which settles very slowly, was washed and decanted several times with gypsum solution to keep it flocculated, and then put on a linen filter. After the liquid had passed, the mass was further washed by shaking up in a bottle with gypsum solution, this operation being repeated until the filtrate was nearly colorless. The precipitate was dried at  $100^{\circ}$ , whereby it lost considerably in volume, forming a hard, brilliant, brittle mass with conchoidal fracture. It was free from ready-formed ammonia expellable by magnesia. The lime-magnesia compound thus prepared naturally contained gypsum. In the air-dried condition the precipitates prepared from two different soils had the following composition :

*West Berkeley Soil.*—An excessively stiff clay or “black adobe” soil, rich in lime, containing over 2 per cent. of *matière noire*.

CALCIUM-MAGNESIUM HUMATE.

	Per cent.
Water .....	17.95
Ash .....	14.34
Organic matter.....	67.71
Nitrogen .....	3.06 of the organic matter.

*Redwood Soil.*—From Marin County (sandy humus soil).

CALCIUM-MAGNESIUM HUMATE.

	Per cent.
Water .....	17.80
Ash .....	15.37
Organic matter.....	68.57
Nitrogen .....	4.01 of the organic matter.

The ash of the latter was soluble in dilute hydrochloric acid, leaving an insignificant white residue. It contained :

	Per cent.
Lime.....	47.07
Magnesia.....	13.65
Phosphoric acid .....	6.15
Potash in noticeable quantity.	

The humate from the Redwood soil, being the richer in nitrogen, was used for the nitrification experiment. Twenty-eight grams humate = 22.8816 grams dry matter with 0.767 gram nitrogen, were mixed in a beaker with 2 kilos of sand taken from drifting sand dunes, a short distance from the ocean near San Francisco; it had been previously ignited, and freed from nitrates by leaching with hydrochloric acid and distilled water.

The material for infection was prepared from soil of the ten-acre tract, Southern California Experiment Station. This soil contains from 1,560 to 12,280 pounds of alkali salts per acre to the depth of 1 foot; up to 23 per cent. of these are nitrates = 0.062 per cent. of the soil. After having been freed from nitrates by washing with distilled water, it was shaken with water, and the turbid liquid filtered through linen; the above mixture was moistened with the filtrate.

The material was kept for two months at a temperature of about 25°. Every other day, with some interruptions, the sand was moistened so that the content of free water amounted to about 2 per cent., stirred up with a glass rod, and thus kept in a mellow, flocculated condition, to facilitate the access of the air. After that lapse of time the moistened sand was mixed thoroughly, and a part of it was dried, weighed, and leached with water. The extract, subjected to the colorimetric determination of nitric acid, showed that 5.94 per cent. of the nitrogen of the humus substance had been nitrified.

Further experiments are in progress for comparing the nitrification in a natural soil, and in the same freed from *matière noire*, in which the microscope showed only slightly browned vegetable débris.

*Conclusions.*—The assumption made heretofore by Prof. Hilgard and others that Grandeau's *matière noire* is a direct source of nitrogen through nitrification, is definitely verified by the above experiment, in which all other possible sources were eliminated. It also justifies, presumptively, Prof. Hilgard's thesis that humus containing a high percentage of nitrogen, such as is found in the soils of the arid regions, will yield larger amounts of nitrates in the same time than will that of lower nitrogen percentages; and that conversely, low nitrogen percentages may fail to supply a sufficiency for plant growth.

*Determination of Humus.*<sup>1</sup>—An investigation was also made to test the Grandeau method for the determination of humus, and particularly that of nitrogen in humus, as hitherto used. The method is the following :

Two portions of 5 or 10 grams of air-dried soil are weighed off into prepared filters. They are treated with 1 per cent. hydrochloric acid to dissolve out the lime and magnesia, as already explained. The treatment with acid is continued until there is no reaction for lime ; the acid is then washed out with water to neutral reaction. The funnels containing the washed soils are now stoppered and one of them is treated with ammonia water (6 per cent.) for the determination of humus by evaporation, and the other with sodium hydroxide (4 per cent.) for the estimation of nitrogen. The lye, whether ammonia or soda, remains in the respective funnels a few hours ; the solution is then allowed to pass through and the filter washed once with the lye ; the funnel is then restoppered and a fresh quantity of the solvent put on the filter. The treatment is repeated until the filtrate remains colorless. The solutions are then made up to 1 liter, and aliquot parts are taken for the determination.

The ammonia solution is evaporated in a weighed platinum dish, the residue dried at 100°, weighed, ignited, and reweighed, the loss in weight showing the amount of humus.

The soda solution is treated with sulphuric acid and mercuric oxide to determine the nitrogen in the usual way.

The percentage of nitrogen in the sodium extract is referred to the percentage of humus in the soil as determined by ammonia extraction, for obtaining the percentage of nitrogen in the humus.

It was to be decided whether, as assumed in this method, ammonia and soda extract the same quantities of humus and nitrogen ; *i. e.*, the same substances. For this purpose two soils, peaty soil from Westminster, Orange Co., Cal., with 19.12 per cent. humus, and heavy black adobe soil from the University grounds with 1.20 per cent. humus, were treated as above described. A duplicate of the Westminster soil served for determining the quantity of humus lost for the analysis by the extrac-

<sup>1</sup> The word "humus," as used in this paper, is intended to designate Grandeau's *matière noire*.



tion with hydrochloric acid and water, which was prolonged until 1 liter of filtrate was obtained. Three hundred cc. of this filtrate on evaporation gave 0.0375 gram residue, containing 0.0367 gram organic matter with 7.45 per cent. nitrogen. This quantity of organic matter is 4.53 per cent. of that contained in the ammonia extract.

For determining the organic matter of the ammonia solution, aliquot parts of it were evaporated. The residue always contains combined ammonia, which was determined in another aliquot part (previously boiled to expel free ammonia) by distillation with magnesia. The quantity found, subtracted from the loss of weight by ignition, gives the organic matter. In the residue from the distillation the organic nitrogen was determined by the Kjeldahl method.

	Gram.
Residue of 200 cc. ammonia solution.....	0.1795
Ash .....	0.0108
Ash-free ammonia humate.....	0.1687
Less combined ammonia.. ..	0.00834
Organic matter.....	0.16036

The combined ammonia taken up from the ammonia solution amounts to 4.93 per cent. of the ash-free ammonia humate; the organic nitrogen, to 6.98 per cent. of the organic matter.

The determination of the organic nitrogen in the ammonia and soda solutions respectively, when applying the above correction, gave the following results:

	Mg.
Organic nitrogen in 100 cc. ammonia solution.....	5.33
Organic nitrogen in 100 cc. soda solution.....	8.23

These results are important in that they prove that soda solution extracts more nitrogen than does ammonia.

On account of the impossibility of determining the organic matter in the neutralized soda solution by evaporation and calcination, because of the large quantity of sodium salt, which hinders the combustion, it was decided to determine by the precipitation of the humus, the quantity and quality of humus-substances in both extracts. In order to determine which reagent precipitates the humus most completely, ammonia-humate extract from University adobe soil was treated with solutions of copper and magnesium sulphates, and with hydrochloric acid. Before adding the salt solutions, the humus

extract was freed from uncombined ammonia by boiling; the precipitates were washed with boiling water, in which the magnesium humate was rather soluble, while the filtrate from the copper humate was perfectly clear and nearly colorless. The hydrochloric precipitates were washed with 2 per cent. hydrochloric acid until 500 cc. had passed. All precipitates were free from ammonia. The nitrogen content of the filter was considered. For all precipitations the same quantity of ammonia extract was used.

	Precipitants used.		
	Copper sulphate.	Magnesium sulphate.	Hydrochloric acid.
Organic matter of the precipitates in per cent.			
of the total organic matter of the extracts	89.16	65.16	85.21
Nitrogen of the precipitates in per cent. of the organic matter of the precipitates.....	....	4.48	4.93
Nitrogen of the precipitates in per cent. of the total organic nitrogen of the extract..	....	....	88.24
Ash in per cent. of the precipitates.....	23.40	14.60	5.21

These results show that magnesium sulphate (because of the solubility of humates in water) is not suitable as a precipitant, while copper sulphate precipitates the humus-substances most completely. Hydrochloric acid has nearly the same complete effect as copper sulphate, and as it can be added to the extract without previous elimination of ready-formed ammonia, it was used for the determinations described above.

The precipitation of the humus with hydrochloric acid in the ammonia and soda extracts from the Westminster and University soils, gave the following results:

				Nitrogen of the precipitates in per cents of	
				the organic matter of the precipitates.	the total organic nitrogen of the extract.
		Precipitate of the humus acids by hydrochloric acid.	Organic matter of the same.		
<i>Westminster Soil—</i>	cc.	Gram.	Gram.		
Ammonia solution..	200	0.1127	0.2110	5.84	54.78
Soda solution .....	200	0.1495	0.1490	3.75	22.78
<i>University Soil—</i>					
Ammonia solution..	300	0.0299	0.0233	....	....
Soda solution.....	300	0.0103	0.0077	....	....

It is thus seen that the humus-substances of these two soils behave altogether differently toward ammonium and sodium hydroxides as solvents.

The nitrogen of these precipitates was not determined on account of the small amounts obtained. The organic matter of the hydrochloric acid precipitate from the Westminster ammonia solution is 70.24 per cent. of the total quantity of organic matter contained in the same.

Even if the chlorides of ammonium and sodium should influence differently the solubility of the precipitates, the ratio of the latter, which is 3 : 4 in the first, and 3 : 1 in the second case, shows that substances of different nature are thus obtained.

*Organic Matter in the Soda Extract.*—For determining approximately the ratio of nitrogen and organic matter in the soda extract, a weaker solution, which, of course, may have a different solvent power, was used in the extraction. 140 grams of University adobe soil, after being extracted with hydrochloric acid and water (250 cc. of the latter contained 0.0133 gram organic matter) was treated during twelve hours with 1 per cent. soda solution, then washed with 0.25 per cent. soda-lye, this operation being repeated until 1 liter filtrate was reached. 50 cc. of this were evaporated, the residue ignited, a solution of ammonium carbonate added in order to convert lime and magnesia into insoluble carbonates, evaporated again, and the residue gently heated. Then the ash was extracted with water and the quantity of sulphuric acid necessary for neutralizing the soda determined by titration. With the same quantity of acid 50 cc. of the soda solution was evaporated. The residue dried, weighed, ignited, and reweighed showed the organic matter. The determination of nitrogen was made with an aliquot part.

For comparison, 140 grams of the same soil were treated with the same quantities of acid, water, and 6 per cent. ammonia, and the extract was analyzed in the usual way. The ash-free residue contained 5.88 per cent. of ready-formed ammonia.

	cc.	Organic matter. Gram.	Organic nitrogen in per cents. of the organic matter.
Ammonia solution.....	50	0.0589	4.73
Soda solution.....	50	0.0543	5.37

These figures, however, do not allow a definite conclusion as to the total amount of soluble humic matter in the soil : for it was found that in the ammonia filtrates obtained at different times during the extraction (which lasted six days), the nitrogen percentages of the organic matter vary considerably. The differences in the percentages of combined, ready-formed ammonia are small.

AMMONIA SOLUTION FROM SOIL FROM THE TEN-ACRE TRACT.

	Organic nitrogen. <sup>1</sup>	Combined ammonia. <sup>2</sup>
Filtrate from the first four hours.....	4.90	6.75
Filtrate from the seventh and eighth day .....	9.35	7.26

Apparently the humus-substances that are poor in nitrogen are readily soluble in ammonia and consequently form the main part of the first extract, while the substance with higher nitrogen percentages are less soluble and need a longer time for entire extraction by ammonia, but are more quickly dissolved by soda.

CONCLUSIONS.

1. By leaching with hydrochloric acid and water a certain quantity of humus, varying in the different soils, is lost to the subsequent extraction with ammonia.

2. The content of nitrogen of the soda extract, being different from that of the ammonia extract, cannot be directly referred to the content of organic matter of the latter.

3. In the determination of organic matter and nitrogen in the ammonia extract, the quantity of combined ammonia must be considered, as has been described in the analysis of Westminster humus.

It is thus evident that the percentages of humus heretofore determined are too high, inasmuch as the combined ammonia, which is about 5 per cent. of the ash-free ammonium humate, has been erroneously calculated as organic matter. Furthermore, if all soils behave like Westminster soil, from which soda extracts about one and a half times as much nitrogen as does ammonia, the nitrogen percentages in humus as heretofore determined, even though they are referred to organic matter and combined ammonia, would be too high.

<sup>1</sup> In per cents. of the organic matter contained in the solution.

<sup>2</sup> In per cents. of the ash-free ammonia humates.

4. The question still remains whether soda or ammonia solution, and in what strength, satisfy best the requirements of a solvent for humus substance, regarded as the sum of organic substances, decomposed or not, that are immediately available for the plants.

After concluding this investigation, we received a publication of A. L. Emery entitled "Soil Humus: Some Sources of Error in Analytical Methods."<sup>1</sup> As to the absorption of ammonia by the humus solution, there mentioned, it is, as we have explained, at least partially a simple process of combination of the humus acids (liberated by hydrochloric acid from earth bases) with the ammonia; the quantity of the latter has been regularly determined by Prof. Hilgard for some time past, by distillation with magnesia (not lime, which decomposes organic nitrogen compounds). A question, however, still to be decided is whether the ammonia used forms amido-compounds with the humus substances during the digestion or evaporation.

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#### NOTES.

*The Brown-Taylor-Richards Method for the Microscopical Identification of Butter.*—In the June number of the Journal appears an article by John A. Hummel on "Brown and Taylor's Official" method of identifying butter, with plates showing the appearance of butter, oleomargarine, and renovated butter, when viewed by polarized light. This is the first time the method used by the Bureau of Internal Revenue for identifying oleomargarine has been formally christened, and I would suggest, if the designation is to stand in chemical literature, the addition of the name of Mr. Richards, formerly microscopist of this office, to whom is due the credit for its adoption and successful employment as a field test for the past twelve years. His report on this subject will be found on page CLXII of the Annual Report of the Commissioner of Internal Revenue for the fiscal year ended June 30, 1888. Directions for the use of the form of (unmounted) microscope officially adopted and its polarizing attachments are given in Series 7, No. 9, revised, of the Regulations of the Internal Revenue Office, everything being simplified as much as possible, so that the test can be performed by

<sup>1</sup> This Journal, 22, 285 (1900).

persons not specially skilled in microscopical manipulation. These regulations, which are in the hands of all internal revenue officers, contain plates prepared by Richards showing the appearance of oleomargarine when viewed by polarized light, presenting the same characteristics as are given by the plates in Hummel's article, except that no reproduction is made of the appearance of butter, since this is, practically, a blank field.

In regard to the use of this test to distinguish between fresh and renovated butter, the experience of this office would tend to substantiate strongly the claims for its value put forth by Hummel. The regulations above referred to recognize the fact that it is really a test for the presence of melted fat, and prescribe that all samples giving a doubtful appearance in the microscope shall be sent in to Washington for a chemical examination. Of those which proved to be butter when thus examined, about nine-tenths are renovated butter, showing a field more or less mottled when examined with crossed nicols. In fact the value of the method as a sorting test to discriminate between butter and oleomargarine has been seriously impaired of late years by reason of the large quantity of renovated butter which has found its way into the markets. This is mainly due, however, to the lack of skill on the part of revenue officers, few of whom have occasion to make frequent use of the instrument. To a person skilled in the use of the polarizing microscope, it is not difficult to distinguish between oleomargarine and melted butter, for it is seldom a sample of the latter is met with which gives the sharply defined, crystalline appearance of the field typical of most oleomargarine. In applying the method to the identification of renovated butter much care should be exercised, for, in my experience, most butters will show *some* variation in the field, due probably to a slight crystallization at some period in their production, and it is rare indeed to find a sample giving the uniformly blank field implied by Hummel's plate of "normal butter."

The method certainly deserves mention along with the tests given by Hess and Doolittle,<sup>1</sup> the best of which is the "spoon test" (the absence of froth in oleomargarine or renovated

<sup>1</sup> This Journal, 22, 150.

butter when heated in an open receptable) which has been in use for the detection of oleomargarine for many years, and which is preferred by some revenue officers to the microscope test.

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*The Analysis of Arsenical Insecticides.*—Since sending my article<sup>1</sup> on "The Adulteration and Analysis of the Arsenical Insecticides" to press I have done still further work on the soluble arsenious oxide in Paris green, and find that although an extraction of 1 gram of Paris green with 500 cc. of water finally gives practically constant results, still a small amount of cupric oxide goes into solution at the same time, thus indicating that either the Paris green itself is soluble in cold water or breaks up slightly on treatment with this medium. I am inclined to think that this last assumption is the more likely, since the amount of copper oxide going into solution in the 500 cc. of water is not constant.

If we assume then that the Paris green breaks up, and that for a certain amount of copper oxide a corresponding amount of arsenious oxide goes into solution, the figure obtained for soluble arsenious oxide (without taking into consideration the breaking up of the Paris green itself) which we will call the *apparent* per cent. of arsenious oxide, will not represent the *actual* per cent. of arsenious oxide, but a determination of the copper oxide dissolved in the water will have to be made, and after calculating how much arsenious oxide this corresponds to, the resulting figure will be subtracted from the *apparent* per cent. of arsenious oxide, thus leaving the *actual* per cent. of free arsenious oxide in the green.

It is of course possible, even probable, that the arsenious and copper oxides of Paris green do not go into solution in water in the same proportion that they are present in the original compound, but in the present state of our knowledge it seems to be the most plausible assumption that they do.

The determination of copper oxide is made by precipitating an aliquot portion of the 500 cc. of cold water extract with hydrogen sulphide, filtering, washing and drying the combined sul-

<sup>1</sup> This Journal, 22, 568.

phides of arsenic and copper, burning the precipitate and filter with powdered sulphur, and finally weighing as the mixed oxide and subsulphide of copper. On ten samples of Paris green the following results were obtained:

No.	Apparent per cent. of arsenious oxide extracted.	Per cent. of copper oxide extracted.	Arsenious oxide corresponding to copper oxide extracted.	Actual per cent. of arsenious oxide in Paris Green.
1.....	5.81	0.80	1.50	4.31
2.....	9.69	0.55	1.03	8.66
3.....	4.60	0.70	1.31	3.29
4.....	4.60	0.60	1.12	3.48
5.....	4.11	0.65	1.21	2.90
6.....	3.63	0.50	0.94	2.69
7.....	7.75	1.35	2.53	5.22
8.....	6.54	0.70	1.31	5.23
9.....	10.65	0.45	0.84	9.81
10.....	5.57	0.90	1.69	4.88

J. K. HAYWOOD.

*On Carborundum.*—In a paper on carborundum (carbide of silicon), read at the World's Congress at Chicago in 1893, and published later in this Journal,<sup>1</sup> there appeared in the second paragraph the following statement :

“ It is an American invention, having been discovered by Edward H. Acheson, of Monongahela City, Pa., who carried the invention to commercial success with extraordinary energy in the face of many obstacles.”

As a part of the discussion at the close of the paper, I asked the author if he was aware that an electric furnace precisely similar to the one he had described was fully protected by letters patent issued to Messrs. Eugene H. and Alfred H. Cowles, in 1884. I further asked him whether the author was aware that in 1885, the substance to which had recently been assigned the name carborundum, was made in the Cowles furnace, and that specimens of this material could be found in several museums throughout the country. The author disclaimed any knowledge of such a furnace, or that any such material had been produced prior to that produced by Mr. Acheson.

In the United States Circuit Court of Appeals for the Third Circuit (Judges Dallas, Gray, and Bradford), a decision has

<sup>1</sup> This Journal, 15, 411.



just been rendered (May 28, 1900) in a case of infringement, in favor of the patent granted to A. H. and E. H. Cowles, Dec. 24, 1884, and against the patent of E. H. Acheson, alluded to above.

In stating the ground of their decision, the judges make the following statement: "There can be no doubt on the evidence that prior to the process patent in suit metallurgical operations had been performed through the instrumentality of the electric arc, electrical conductors consisting of wires or rods of metals, or of other solid or concrete bodies, or by electrolysis. But on careful examination we have failed to find any patent, publication, or other matter alleged as an anticipation, or as showing the prior art, a practical process for metallurgical or analogous operations involving the use of a discrete body of conductive, but resistant material rendered incandescent by the passage of an electric current, and mixed or otherwise in contact with the material to be treated. This is the broad, underlying idea of the process patent in suit, and is covered by its claims. The Messrs. Cowles were the first to invent and use this process, and the patent must be sustained. It is a meritorious one, and its claims are entitled to considerable liberality of construction." This decision gives priority broadly to the Messrs. Cowles for reducing ores and other substances by the incandescent method.

CHARLES F. MABERY.

CLEVELAND, June 5, 1900.

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## NEW BOOKS.

THE CHEMISTRY OF THE METALS. BY J. H. KASTLE. Lexington, 1900. vi + 198 pp. 8vo.

The author of this book admits in his preface that the number of text-books on general chemistry is so great that "the burden of proof certainly rests upon any new writer who ventures into this field to show that anything new in this line is deserving of publication," and makes a plea for the fuller study of the metals, bodies that constitute two-thirds of the elements. The author says: "An attempt has been made to supplement the laboratory work on each family of metals with a general presentation of the subject according to the Periodic Law."

Chapter I opens with general elementary statements as to the

differences between mixtures and compounds, analysis, synthesis, and chemical study of a substance; in successive chapters are given descriptions of the metals taken by families and by groups so as to avoid unnecessary duplication, extending from the alkalis to iron, nickel, and cobalt. Following the descriptive portion of each chapter are sections prescribing "Laboratory Work;" these sections consist chiefly of series of questions and in them lies the principal claim to originality for the volume. The queries are intended to make students think for themselves, but sometimes are singularly elementary; thus, following several pages describing the character of the metal magnesium, students are asked—"Is magnesium a metal?" "Is it heavy or light?" "What is its color?" (p. 47). After comparing granite and mercuric oxide, students are asked—"How could you make mixtures?" Yet some of the queries are difficult and would require examination of larger treatises.

To use this volume for instruction, the students must have previously become acquainted with the gaseous elements, the principal acids of inorganic chemistry and the rudiments of qualitative analysis, yet the primary principles of chemistry are laid before them with minutiae that would seem unnecessary had they mastered them previously. At the same time students are directed to make certain experiments, and the instructions given are hardly sufficient. On page 5, for example, students are told to heat  $\text{HgO}$  in a hard glass tube and to collect the gas evolved over water, but how to arrange this is not mentioned, nor is there any wood-cut of apparatus to illustrate the operation; indeed, illustrations are entirely wanting throughout the volume.

A blemish in the manufacture of the book is due to the carelessness of the printer; paper of uniform color and glaze is not used throughout; page 112 is of a bluish tint, and page 113 of a decided yellow hue. There is no index.

H. CARRINGTON BOLTON.

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### ERRATA.

In Vol. 22, page 573, line 23, for "sodium acetate" read "sodium arsenate;" page 576, line 28, for "really" read "nearly."

## THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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[CONTRIBUTION FROM THE NORTH CAROLINA AGRICULTURAL EXPERIMENT  
STATION.]

METHODS OF DETERMINING PROTEID NITROGEN IN  
VEGETABLE MATTER.

BY G. S. FRAPS AND J. A. BIZZELL.

Received August 10, 1900.

THE method usually used for the determination of proteid nitrogen, is that modification of the Ritthausen method proposed by A. Stutzer,<sup>1</sup> which consists in precipitating the proteids with copper hydroxide, and determining the nitrogen in the precipitate. This method has been adopted by the Association of Official Agricultural Chemists, and is in use by chemists generally.

Mallet<sup>2</sup> has recently proposed that the proteids be precipitated with phosphotungstic acid at 90° C., using in addition tannic acid when peptones are present.

Wiley<sup>3</sup> determines the proteids in animal materials by precipitating them with bromine.

The work here to be described is a study of the applicability of phosphotungstic acid and bromine as precipitants for the proteids of vegetable materials.

<sup>1</sup> *Jour. f. Landw.*, 28, 103.

<sup>2</sup> Bull. 54, Division of Chemistry, U. S. Dept. of Agr.

<sup>3</sup> Bulletin 54, Division of Chemistry, U. S. Dept. of Agr.

## THE PHOSPHOTUNGSTIC ACID METHOD.

The method as proposed by Mallet is, briefly, as follows: The sample is digested with hot water, filtered on a nitrogen-free filter, and washed with hot water containing a little free acid so long as it gives up soluble matter in sensible amount. It is not advisable to use hot water at first when much starch is present. The filtrate is made slightly acid with acetic acid, heated to about  $90^{\circ}$ , and filtered. To the second filtrate an acidified solution of phosphotungstic acid is added so long as a precipitate continues to be formed, avoiding any large excess of reagent, the liquid heated to about  $90^{\circ}$ , filtered, and the precipitate washed with water of about the same temperature. The nitrogen in the precipitates is determined by the Gunning-Kjeldahl method, and calculated to proteids. When peptones are present they are precipitated with tannic acid from the solution which has been acidified with acetic acid. When proteoses are present it may be well to make a check determination of their amount by saturation of the aqueous solution, after acidification with acetic acid, heating and subsequent cooling, with zinc sulphate, and determining nitrogen in the precipitate. It may be well to remove fat when it is present in large quantity.

## METHOD MODIFIED.

The method above described involves three, or, if peptones are present, four filtrations, which make it very long and tedious. The object of the precipitation with acetic acid is to reduce the bulk of the subsequent phosphotungstic acid precipitate, out of which the amides are to be dissolved by hot water. Its use is unnecessary. When the above method was followed it was found impossible to get a clear filtrate from most of the vegetable materials tested, although various modifications were tried. At  $60^{\circ}$ , however, no such difficulty was encountered, although at a slightly higher temperature—depending on the material—turbidity would begin to appear. It was also found that between  $60^{\circ}$  and  $100^{\circ}$ , a considerable portion of the nitrogen goes into solution. For this reason the temperatures of  $60^{\circ}$  and  $100^{\circ}$  were selected for further tests,  $100^{\circ}$  giving the maximum turbidity and minimum amount of nitrogen,  $60^{\circ}$  the minimum of

turbidity, *i. e.*, a clear filtrate. The method after much experimentation was simplified as follows: 1.4 grams of the substance in a beaker were stirred well with 100 cc. water, the phosphotungstic acid reagent added and the liquid heated. The liquid was kept at the desired temperature (60° or 100°) for fifteen minutes, filtered, the precipitate washed with water at the same temperature, and nitrogen determined in it.

The reagent used was a 5 per cent. solution of phosphotungstic acid in 2.5 per cent. hydrochloric acid; 5 cc. were used for 3 per cent. or less of nitrogen, 10 cc. for 6 per cent., and 15 cc. for 9 per cent.

#### EFFECT OF REAGENT.

In dealing with vegetable materials it was found impossible to tell when a slight excess of the phosphotungstic acid reagent had been added. The following results were obtained by using different quantities of the reagent, and heating to 60°. The figures are means of two closely agreeing determinations.

##### No. 1. COTTONSEED MEAL.

	Nitrogen. Per cent.
10 cc. reagent.....	6.61
30 " " .....	6.64
50 " " .....	6.27

##### No. 2. WHEAT BRAN.

5 cc. reagent.....	2.07
10 " " .....	2.08
25 " " .....	2.11
45 " " .....	2.09

##### No. 3. COWPEA MEAL.

5 cc. reagent.....	3.18
10 " " .....	3.11
25 " " .....	3.22
45 " " .....	3.17

A small excess of reagent does not affect the results. A very large excess affects them in the case of cottonseed meal. It seems that 5 cc. of the reagent are sufficient for any vegetable material containing less than 3 per cent. of nitrogen, 10 cc. for 6.5 per cent., and 15 cc. for 9 per cent.

#### EFFECT OF TEMPERATURE.

As has already been stated, a clear filtrate could not, as a rule,

be obtained at a temperature much over  $60^{\circ}$ , and nitrogen goes into solution between  $60^{\circ}$  and  $100^{\circ}$ . In cottonseed meal and wheat bran, the greatest amount of solution takes place between  $75^{\circ}$  and  $90^{\circ}$ ; cottonseed meal gave at  $60^{\circ}$ , 6.61 per cent. nitrogen; at  $75^{\circ}$ , 6.58 per cent.; at  $90^{\circ}$ , 4.94 per cent.; at  $100^{\circ}$ , 4.22 per cent. Wheat bran at  $60^{\circ}$  gave 2.08 per cent. nitrogen; at  $75^{\circ}$ , 2.01 per cent.; at  $100^{\circ}$ , 1.75 per cent. The amount of nitrogen dissolved between  $60^{\circ}$  and  $75^{\circ}$  is very small.

In order to show the solvent action between  $60^{\circ}$  and  $100^{\circ}$ , the following figures are given. Of the nitrogen precipitated at  $60^{\circ}$ , in cottonseed meal (No. 1.), 36 per cent. goes into solution at  $100^{\circ}$ ; another sample (No. 2.), 24 per cent.; still another (No. 3.), 21 per cent.; cowpea meal, 9 per cent.; green peas, 7 per cent.; soy beans, 18 per cent.; horn meal, 9 per cent.; linseed meal, 12 per cent.; and dried blood, 47 per cent.

Working with blood at  $100^{\circ}$ , it was found that 5.97 per cent. (37.31 per cent. proteids) goes into solution between  $60^{\circ}$  and  $100^{\circ}$ . This sample of blood contained 13.66 per cent. nitrogen, 13.39 per cent. of it being insoluble in water. The filtrate from  $100^{\circ}$  phosphotungstic acid method was clear, and remained clear although 5.97 per cent. of proteid nitrogen was therein dissolved. This observation threw doubt upon the basis upon which the phosphotungstic acid method is founded; namely, that the phosphotungstic acid precipitate with proteids is not soluble in hot water. This statement is based upon the observation that "the supernatant liquid remained clear on being heated along with the precipitate and subsequently cooled". The following experiments confirmed this suspicion, and proved that phosphotungstic acid does not completely precipitate proteids at  $90^{\circ}$  or  $100^{\circ}$ .

0.35 gram of the materials named below were placed in a Kjeldahl flask, 100 cc. of water and 5 cc. of the phosphotungstic acid reagent added, and the solution heated to  $60^{\circ}$ . The solution was kept at this temperature for fifteen minutes, filtered, washed with water at the same temperature, and nitrogen determined in the precipitate by the Gunning method. Determinations were also conducted at  $90^{\circ}$  and  $100^{\circ}$ . Those at  $90^{\circ}$  were conducted as the others except that the filtration was proceeded with as soon as that temperature was attained.

Name of material.	Total nitrogen. Per cent.	Nitrogen. 60° phosphotung- stic acid method. Per cent.	Nitrogen. 90° phosphotung- stic acid method. Per cent.	Nitrogen. 100° phosphotung- stic acid method. Per cent.
Casein.....	14.12	14.24	13.24	13.34
Blood albumen .	11.82	11.74	11.26	9.92
Egg albumen...	12.42	12.58	12.38	11.90
Haemoglobin ...	13.40	12.82	11.28	9.20
Blood fibrin ....	13.94	13.62	....	12.60
Gelatin.....	14.98	....	12.90	11.52

It will be noted that in every case the proteid precipitate was partially dissolved when it was heated. The phosphotungstic acid reagent therefore is of no value for precipitating proteids at 90° or 100°. At 60°—excepting gelatin, and perhaps haemoglobin,—the proteids seem to be completely precipitated.

COMPARISON OF THE MODIFIED PHOSPHOTUNGSTIC ACID AND  
THE STUTZER METHODS.

The 60° phosphotungstic acid method has already been described. The following table contains some results obtained by this method together with determinations made by the Stutzer method. The figures are means of two determinations :

Name of material.	Total nitrogen. Per cent.	Nitrogen. 60° phosphotungstic acid method. Per cent.	Nitrogen. Stutzer method. Per cent.
Wheat bran .....	2.20	2.07	1.79
Corn bran .....	1.54	1.48	1.38
Waste rape .....	3.57	2.32	2.62
Green peas .....	1.76	1.57	1.45
Linseed meal .....	2.86	2.74	2.62
Cottonseed meal No. I ..	6.80	6.61	6.51
“ “ No. II .	6.18	6.24	6.17
“ “ No. III.	6.62	6.48	6.42
Dried blood .....	13.66	12.82	13.00
Soy beans .....	6.15	5.90	5.97
Horn meal .....	14.70	13.50	13.00
Cowpea meal .....	3.32	3.18	3.19

It will be noted that this method gives results which are, as a rule, almost identical with those by the Stutzer method, although slightly higher. The mean difference is +0.06 per cent., with a maximum of +0.50 per cent., and a minimum of —0.30 per cent. Neither method gives good results with blood; the filtrate from blood by the 60° phosphotungstic acid method

contained 0.57 per cent. water-insoluble nitrogen, and gave a reaction (with copper sulphate and caustic soda) for proteids, and the copper hydroxide dissolved 0.39 per cent. of water-insoluble protein. With regard to the other materials it is impossible to say which method is correct. The 60° method promises, however, to be of value. It is possible that the determination might be carried on at a slightly higher temperature than this, but hardly over 80° in any case.

#### PRECIPITATION WITH ZINC SULPHATE.

A comparison was made between the nitrogen precipitated by zinc sulphate and that by the other methods on a few materials. The method was as follows: 1.4 grams of the substance were heated with 100 cc. of water to boiling, allowed to cool, 2 cc. of dilute sulphuric acid (1:4) and 140 grams crystallized zinc sulphate added. It was allowed to stand a day or more, with frequent stirring, filtered, and washed with a saturated solution of zinc sulphate containing 1 cc. of the dilute acid in 50 cc.

Name of material.	Nitrogen insoluble in zinc sulphate. Per cent.	Nitrogen. Stutzer method. Per cent.	Nitrogen. 60° phosphotungstic acid method. Per cent.
Cottonseed meal .....	6.45	6.51	6.61
Soy beans.....	6.07	5.97	5.90
Blood .....	13.48	13.00	12.82
Cowpea meal.....	3.26	3.19	3.18

The results are higher than by the other methods in three of the four cases, and seem to point to the Stutzer method as being more nearly correct.

#### EXTRACTION OF WATER-SOLUBLE NITROGEN.

Extraction of a vegetable material with hot water sometimes gives discordant results, as was the case with cottonseed meal. The extraction was performed as follows: 1.4 grams were placed in a beaker with 50 cc. water, stirred well, and allowed to stand one hour. The liquid was decanted through a filter, 50 cc. water added to the residue in the beaker, heated to boiling, filtered, and the residue washed with boiling water. The undissolved nitrogen was, in case (a) 4.54 and 4.68 per cent., mean 4.61 per cent.; in case (b) (6 months later) 4.12 and 4.22 per cent., mean 4.17 per cent.; and case (c) (volume of filtrate



less than in case (b)) 5.55 and 5.67 per cent., mean 5.61 per cent. There is thus a variation of 1.44 per cent. of nitrogen, or 9 per cent. of protein. It is quite possible that had the extracting water been slightly acid the results would have been more uniform.

#### THE BROMINE METHOD.

Rideal and Stewart<sup>1</sup> have proposed to use bromine as a precipitant for gelatin. Allen and Searle<sup>2</sup> applied the method to the analysis of meat extracts. Wiley<sup>3</sup> has proposed the following method for the determination of proteids in animal matters. About 1 gram of the dried animal matter is washed with ether by decantation, using from 50 cc. to 100 cc. ether, and decanting through a filter which is to receive the portion insoluble in hot water. After allowing the ether to evaporate, the sample is washed by decantation, first with cold water and then with hot water, the total filtrate being from 300 cc. to 400 cc. The undissolved residues are brought on the filter with the last portions of water and the nitrogen in the residues determined by the Gunning-Kjeldahl method. The filtrate from the insoluble portions is received in Kjeldahl flasks, acidulated with 2 or 3 drops of strong hydrochloric acid, and then about 2 cc. of liquid bromine are added, and the contents of the flask shaken vigorously. Bromine is added until about 0.5 cc. remains undissolved and the supernatant liquid is thoroughly saturated. After standing over night, it is filtered and washed by decantation, the globule of bromine serving to saturate the wash-water. The filter with the precipitate is returned to the flask in which precipitation has taken place, and the nitrogen therein determined by the Gunning method.

#### METHOD MODIFIED.

After some experimentation the method above described was modified for vegetable materials as follows: 200 cc. of water were added to 1.4 grams of the substance in a Kjeldahl flask, heated to boiling, and allowed to cool. It was then acidified with hydrochloric acid, and bromine added until a small globule remained undissolved, the liquid allowed to stand over night,

<sup>1</sup> *Analyst*, 22, 228.

<sup>2</sup> *Ibid.*, 22, 258.

<sup>3</sup> Bulletin 54, Division of Chemistry, U. S. Dept. of Agr.

filtered, and the precipitate washed by decantation, keeping the wash-water saturated with bromine. The filter and precipitate were returned to the flask, and the nitrogen therein determined by the Kjeldahl method.

#### COMPARISON OF THE BROMINE AND STUTZER METHOD.

Proteid nitrogen was determined in a number of materials by the method just described, and the results compared with those obtained by the Stutzer method. The following table contains the results:

Name of material.	Nitrogen. Stutzer method. Per cent.	Nitrogen. Bromine method. Per cent.
Corn silage.....	0.68	0.67
Crabgrass hay.....	1.38	1.51
Green peas.....	1.45	1.25
Cattail millet.....	1.34	1.10
Linseed meal.....	2.62	2.37
Corn bran.....	1.38	1.11
Wheat bran.....	1.79	1.51
Dried blood.....	13.00	12.53
Cowpea meal.....	3.19	2.53
Sheep excrement.....	2.79	2.13
Soy beans.....	5.97	5.23
Green rape.....	2.62	1.84

The bromine method is not applicable in the case of cottonseed meal. In one case the meal was extracted with water, and the extract gave a precipitate which settled almost immediately and contained 0.51 per cent. nitrogen. A duplicate determination gave a turbid liquid, which would not filter clear after standing over night, and when the precipitate finally settled it yielded only 0.10 per cent. nitrogen. When the meal was treated directly with bromine a turbid liquid was formed which refused to filter clear and the precipitate contained varying amounts of nitrogen. The results by the bromine method with two exceptions, are lower than with the Stutzer or the phosphotungstic acid methods. Until it has been proved that bromine precipitates all vegetable proteids quantitatively, which is doubtful, this method must be condemned.

#### THE STUTZER METHOD.

The Stutzer method used in this work is as follows: place 0.7

gram of the substance in a beaker, add 100 cc. water, heat to boiling, or, in case of substances rich in starch, heat on the water-bath ten minutes; add a quantity of copper hydroxide mixture containing about 0.5 gram of the hydroxide; stir thoroughly, filter when cold, wash with cold water and without removing the precipitate from the filter, determine nitrogen adding sufficient potassium sulphide solution to completely precipitate all copper and mercury. If the substance examined consists of seeds, or seed residues, or anything else rich in alkaline phosphates, add a few cubic centimeters of a concentrated solution of alum before adding the copper hydroxide and mix well by stirring.

Several objections have been made to this method. It has been stated<sup>1</sup> that, in some cases, working with a proteid alone, the copper compound underwent partial solution, a blue liquid being formed, although care had been taken to avoid the presence of free alkali. The proteids acting in this way were not named. Another objection has been founded on "the very slight solubility of the copper salts of some of the simpler amido-acids, especially leucin and glutamic acid; in a less degree the same statement applies to aspartic acid. Even at the temperature of boiling water the copper compounds of these substances are but very sparingly soluble, and if the liquid after digestion with cupric hydroxide, be filtered cold,<sup>2</sup> the compounds in question will, if present, be almost certainly left on the filter along with the proteid material."

Laszczynski<sup>3</sup> also states that copper hydroxide precipitates the albumen of wort and beer completely, but also partly precipitates the albumoses and amides.

The copper salt of leucin is soluble in 3,045 parts of cold water and 1,460 parts of boiling water (Beilstein). When 0.7 gram of the substance and 100 cc. of water are used, for any of this salt to remain on the filter, 0.033 gram must be present, or 0.026 gram of leucin (since it contains 19.5 per cent. copper) which would be 3.7 per cent. The copper salt of glutamic acid is soluble in 3,400 parts of cold water and 400 parts of boiling water, and 0.029 gram must be present before any will separate

<sup>1</sup> Bulletin 54, Division of Chemistry, U. S. Dept. of Agr.

<sup>2</sup> Bulletin 46, Division of Chemistry, U. S. Dept. of Agr. (1895), p. 25.

<sup>3</sup> *Analyst* (Abs.), 24, 184.

from 100 cc. water, equal to 0.022 gram glutamic acid, or 3.1 per cent. The solvent action of wash-water is left out of consideration.

When the material contains less than 3.7 per cent. leucin, or 3.1 per cent. of glutamic acid, there is no danger of the amide separating in the cold. But the limits are much higher than these. The solubilities above noted are for the pure salts in pure water. E. Schulze<sup>1</sup> emphasizes the fact that the copper salts of these amides are much more soluble when impurities are present. While the copper salts of aspartic acid and glutamic acid separate quickly from a pure solution, from a mixture of the two they separate very slowly, or not until the liquid has been evaporated.

It is probably better, however, to conduct the determination in a hot solution.

It has also been objected to this method, that albumoses are not precipitated. This objection might be overcome by the use of tannic acid to precipitate them. The tannic acid should be used after the precipitation with copper hydroxide. It is only in rare cases that its use would be necessary. Qualitative tests with tannic acid were made on the filtrates from cottonseed meal, wheat bran, cowpea meal, corn bran, cattail millet, excrement from crabgrass hay, waste rape, excrement from waste rape, and corn silage. A small precipitate was formed in all cases except with cattail millet and corn silage. The precipitate from cowpea meal and corn bran dissolved when the liquid was heated, reappearing on cooling. A repetition of the experiment showed that the precipitate did not always appear with the same material. A determination of nitrogen in the precipitate from cottonseed meal gave 0.03 per cent.—practically none.

#### CONCLUSIONS.

Phosphotungstic acid does not precipitate proteids completely at 90° or 100°.

Phosphotungstic acid at 60° precipitates very nearly the same quantity of nitrogen (with vegetable materials) as copper hydroxide.

Extraction of proteids with hot water does not always give concordant results.

<sup>1</sup> *Landw. Versuch-Stat.*, 6, 220 (1880).

Bromine is not a suitable precipitant for proteids in vegetable materials.

The Stutzer method seems to be the method open to the fewest objections.

Acknowledgment is due Mr. H. W. Primrose, formerly assistant chemist, for assistance in the analytical work.

The above investigation was carried out in the laboratory of the North Carolina Agricultural Experiment Station with the permission of Professor W. A. Withers, chemist.

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## DETERMINATION OF CARBON IN FERROCHROME.

BY A. A. BLAIR.

Received August 14, 1900.

THE method in general use for the determination of carbon in ferrochrome may be briefly described as follows: Place 1 gram of the finely ground ferrochrome in a porcelain or platinum boat with 25 grams of fused potassium bisulphate and insert the boat in a porcelain tube in a gas furnace. Fit each end of the tube with a rubber stopper carrying a glass tube, and fill the forward part of the tube with lumps of cupric oxide. Connect the tube in the forward stopper with a U-tube containing strong sulphuric acid and chromic acid, a second U-tube containing dry pumice, a third containing dried, not fused, calcium chloride, the weighed absorption apparatus, and a guard tube. Connect the tube in the rear stopper with sources of purified oxygen and air. Start the oxygen through the apparatus and heat the tube carefully, beginning at the forward end which contains the oxide of copper, until the entire length of the tube inside the furnace is at a dull red heat in order to fuse the contents of the boat. Replace the oxygen with air, detach and weigh the absorption apparatus.

This does not seem very troublesome, but in practice several difficulties arise that make the method not only unsatisfactory, but very unreliable.

The sulphuric acid, both that evolved from the potassium bisulphate as sulphuric acid, and that evolved as sulphurous acid and oxidized to sulphuric acid by the oxide of copper and oxygen, acts on the rubber stoppers and sometimes carbonizes them

sufficiently to give results several times greater than the actual carbon content of the ferrochrome. The spattering of the bisulphate, no matter how carefully the heat is applied, generally covers the inside of the tube around the boat and cements boat and tube together. The absorption of sulphuric acid by the oxide of copper causes the latter to swell, usually breaking the tube in the second, and sometimes while it is cooling, in the first determination.

To avoid these difficulties and sources of error, I have devised the apparatus shown in the cuts.

Fig. 1 shows the platinum boats and cover. The smaller

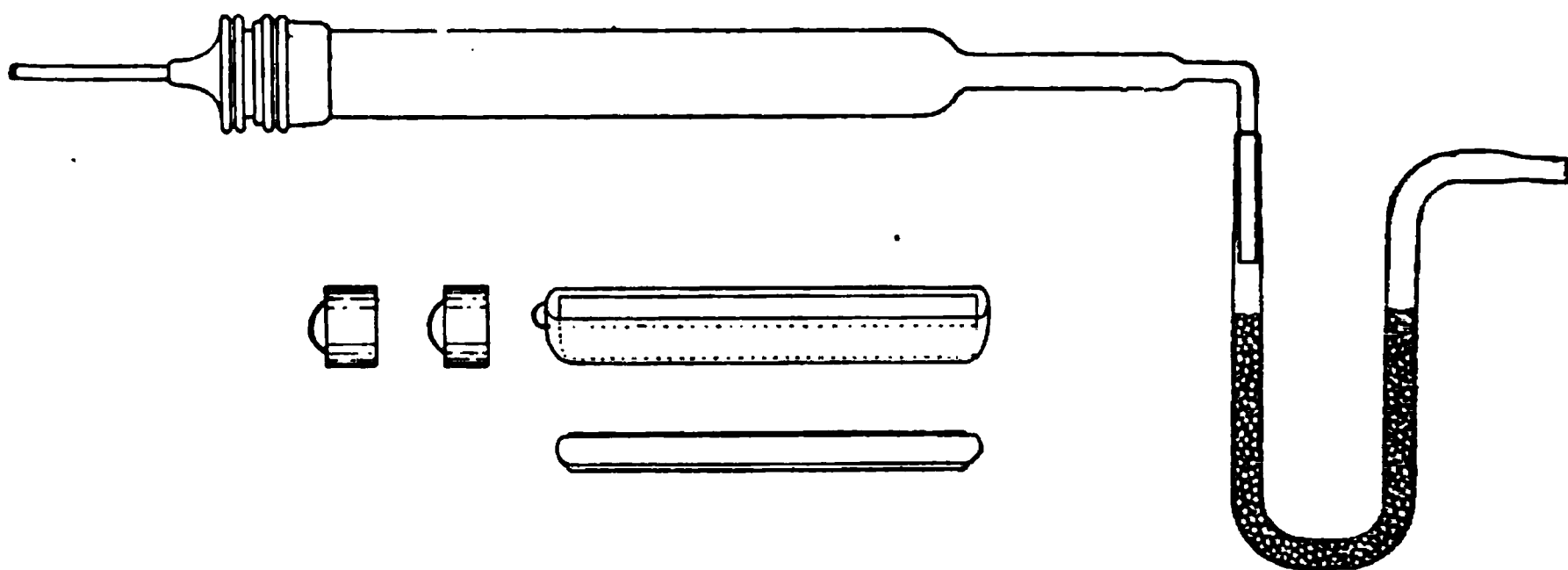


Fig. 1.

boat, 150 mm. long and 25 mm. wide, fits inside the larger and the cover is so arranged that any particles from the melting mass thrown on it run into the larger boat and thus keeps the tube itself perfectly clean.

The platinum tube, shown also in Fig. 1, is 400 mm. long and 30 mm. in diameter and is closed with a ground joint at the rear. The forward end for a distance of 75 mm. is contracted to 12 mm. and filled with platinized asbestos. It is then further contracted to 6 mm. in diameter, and a piece of glass tubing filled with glass beads is fused to it after it is bent downwards at an angle of  $90^\circ$ . The platinized asbestos facilitates the oxidation of the sulphurous acid evolved from the fused mass. The plugs are made of pumice wrapped with platinum foil, and are pushed in after the boat. They serve to fill the back end of the tube and prevent the diffusion of the evolved gases and consequent condensation of sulphuric acid around the ground joint.

Fig. 2 shows the general arrangement of the apparatus. The purifying apparatus for oxygen and air is shown in detail in Fig. 3. The tubes A and B contain respectively potassium hydroxide and concentrated sulphuric acid. It is almost impossible with this form of tube to throw out the contained liquid either forward or backward. In Fig. 2, A is the platinum tube, and B the glass tube containing beads fused to the contracted end of the platinum tube at C. D, D are glass flasks containing a solution of 150 grams of chromic acid and 300 cc. of strong sulphuric acid to the liter. These flasks stand on a copper plate and are heated by a Bunsen burner. The solution serves to oxidize any sulphurous acid that may have escaped oxidation in the contracted part of the platinum tube. E is a U-tube filled with glass beads, and acts as a condenser; F contains pumice saturated with chromic acid, and G contains dried calcium chloride. The absorption apparatus and guard tube follow. The latter is connected by a rubber tube with the gasometer, shown in the cut, which acts as an aspirator and serves to relieve the pressure in the apparatus, which, on account of the condensation of strong sulphuric acid in the tube B and the high spe-

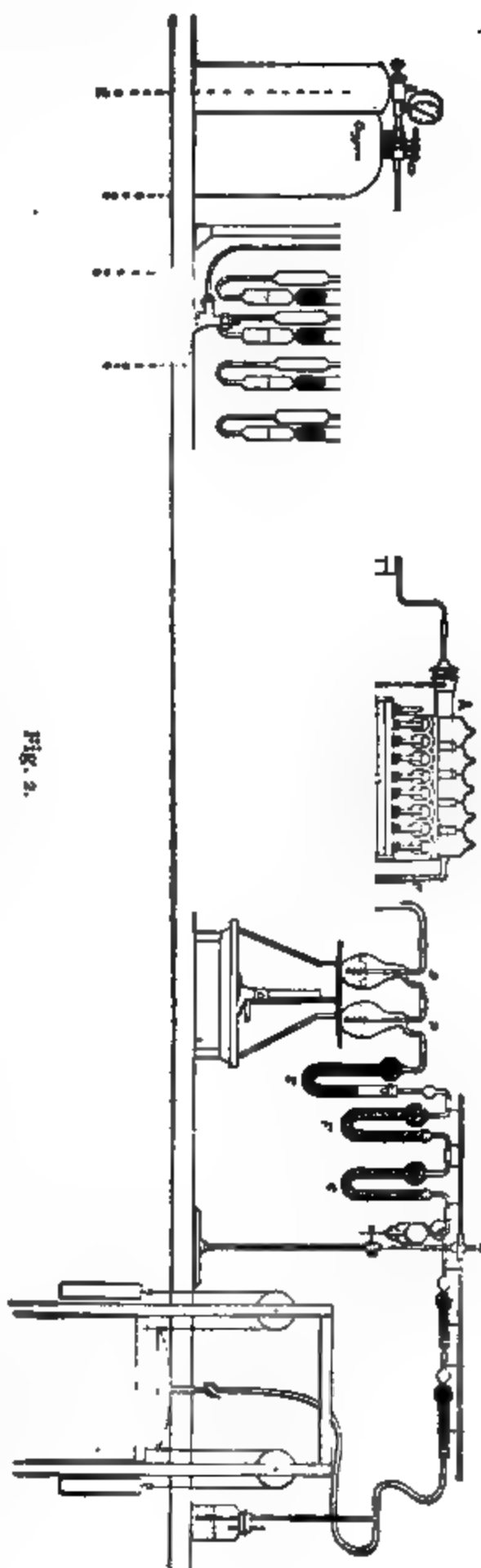


Fig. 2.

cific gravity of the liquid in the flasks D, D, would otherwise be excessive. The details of this connection are shown in Fig. 4.

The method is as follows: Place 25 grams of pure potassium bisulphate in the small boat (Fig. 1), and fuse it over a Bunsen burner or blast-lamp to destroy any carbonaceous matter and allow it to cool. When cold spread 1 gram of the finely ground sample evenly over the surface of the fused mass, place the boat

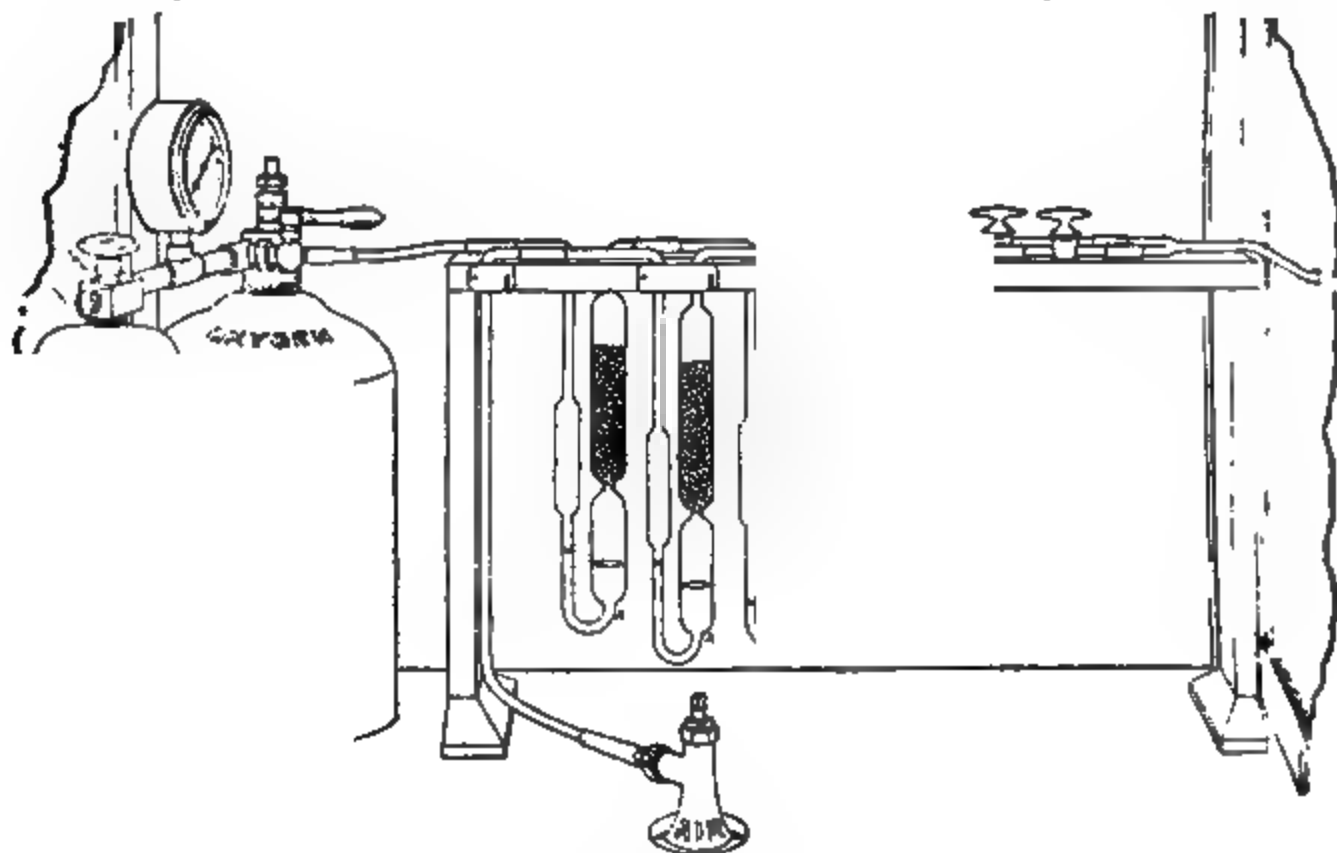


Fig. 3.

inside the larger boat, arrange the cover, place the boats in the tube, insert the plugs and close the tube with the ground joint. Connect the apparatus as shown in Fig. 3, and start a slow current of oxygen through the apparatus. Light the burners under the forward end of the tube which contains the platinized asbestos, and when this is red hot light the burner under the forward end of the boat and light the others successively until the tube is red hot for its entire length where the boat rests. Keep the tube hot for twenty minutes, replace the oxygen with air, turn out the lights, allow the air to run about thirty minutes and detach and weigh the absorption apparatus with the usual precautions.

As a large amount of sulphurous acid is produced it is neces-



sary to heat the tube very gradually in order to keep an excess of oxygen in the tube to oxidize all the sulphurous acid. As the sulphuric anhydride does not condense readily, a slow cur-

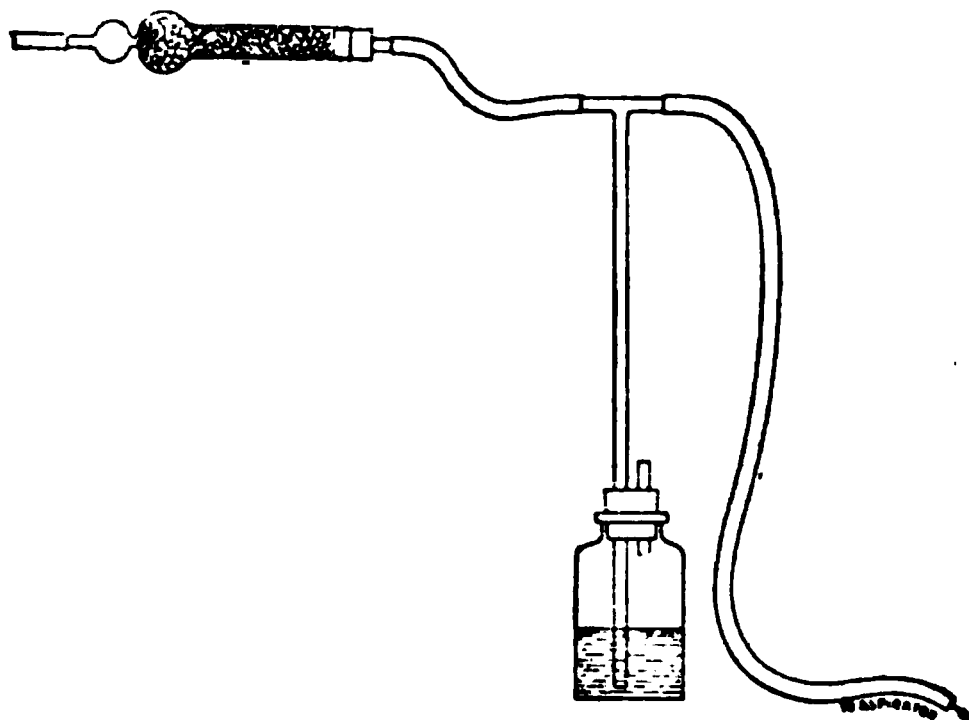


Fig. 4.

rent of gas is requisite, and a combustion requires about two hours and a half.

At the end of the operation the tube is opened and the plugs and boats removed. The fused mass is readily removed from the boats which, with the cover, are washed and ignited, ready for another combustion. About three determinations can be made in a day. Duplicate determinations agree within 0.01 per cent.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 51.]

## THE ELECTROLYTIC OXIDATION OF TOLUENE.

BY AARON MERZBACHER AND EDGAR F. SMITH.

Received September 7, 1900.

THE oxidation of toluene by electrolytic oxygen has been tried by Jos. H. James.<sup>1</sup> The products were a minute quantity of liquid, with an ester-like odor, and a resin, together with unaltered toluene.

Our attention has been attracted to this interesting subject and we have repeated the experiments, varying the conditions, of course, with the hope of finally changing the methyl side-chain to carboxyl.

The apparatus used in the electrolysis was similar to that

<sup>1</sup> This Journal, 21, 890.

generally employed in electrolytic oxidations: a large beaker glass in which stood a porous cup containing the anode liquor, and separating it from the cathode liquor. The porous cup was provided with a rubber stopper, carrying a condenser. The cathode liquor was either a 15 per cent. acid or alkali solution. Ordinary alcohol served as solvent for the toluene.

*Experiment 1.*—The conditions were as follows:

Toluene .....	10 grams.
Concentrated sulphuric acid .....	5 cc.
Water .....	50 cc.
Alcohol .....	150 cc.
N.D. <sub>100</sub> .....	1.1 A.
Volts .....	3.7
Temperature .....	40° C.
Time .....	7 hours.

As the action progressed the liquor assumed a dark yellow color. Upon examination, at the expiration of the oxidation period, unaltered toluene and a little resin were found present.

*Experiment 2.*—Acetone was substituted for the alcohol and the conditions were:

Toluene .....	10 grams.
Concentrated sulphuric acid .....	5 cc.
Water .....	75 cc.
Acetone .....	175 cc.
N.D. <sub>100</sub> .....	1.1 A.
Volts .....	3.5
Temperature .....	35°
Time .....	6 hours.

The anode liquor was carefully searched for new products: toluene and a little resin represented all that could be discovered.

*Experiment 3.*—An alkaline liquor was substituted for the acid of the two preceding experiments. The conditions were:

Toluene .....	10 grams.
Alcohol .....	110 cc.
Water .....	50 cc.
Sodium carbonate .....	5 grams.
N.D. <sub>100</sub> .....	0.54 A.
Volts .....	14
Temperature .....	40° C.
Time .....	3 hours.

Carbon dioxide was conducted through the cathode liquor

during the experiment. Very little of the toluene was changed. Resin was formed but nothing definite could be extracted from it.

*Experiment 4.*—A return to an acid solution will be observed in this experiment. Larger quantities of material were also used. The conditions were:

Toluene .....	55 grams.
Alcohol .....	190 cc.
Concentrated sulphuric acid .....	15 cc.
Water .....	15 cc.
N.D. <sub>100</sub> .....	1.1–1.6 A.
Volts .....	5–26
Temperature .....	20°–33° C.
Time .....	12 hours.

The anode liquor had the odor of benzaldehyde, and apparently that of ethyl benzoate. Three grams of resin were obtained. The fraction, boiling at about 213° C., was saponified with caustic potash, and the solution acidified with hydrochloric acid. The product, which separated, was recrystallized from ether. It melted at 121° C., and showed the characteristic tests of benzoic acid. The oxidation of toluene to benzoic acid had, therefore, really taken place, but in the presence of sulphuric acid and alcohol, ethyl benzoate (b. p. 213°) was formed. The quantity of the latter was not very great. The oxidation was far from being quantitative.

Another fraction, obtained from the anode liquor, boiled at 110°–190°. Phenylhydrazine was added to it. The hydrazone, which separated, was purified, when it melted at 150°, the melting-point of the hydrazone of benzaldehyde.

Additional experiments were made; the products were *resin*, *benzaldehyde*, and *ethyl benzoate*. The tests for the last two bodies were unmistakable. The gases evolved in these oxidations were carbon dioxide and oxygen.

The oxidation of ethyl benzene, under conditions similar to those last mentioned for toluene, gave some resin, ethyl benzoate, benzaldehyde, and a small fraction containing an aldehyde other than the latter, but in such slight amount that it could not be definitely identified.

It is proposed to attempt the electrolytic oxidation of the xylenes and of mesitylene.

[CONTRIBUTION FROM THE LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

## LECTURE EXPERIMENTS ILLUSTRATING THE ELECTROLYTIC DISSOCIATION THEORY AND THE LAWS OF THE VELOCITY AND EQUILIBRIUM OF CHEMICAL CHANGE.

BY A. A. NOYES AND A. A. BLANCHARD.

Received September 20, 1900.

### INTRODUCTION.

THE experiments to be described in this paper were originally devised as an accompaniment to an extended course of lectures on theoretical chemistry.<sup>1</sup> Most of the principles illustrated are, however, of such fundamental importance that they must soon be generally introduced even into elementary lecture courses on inorganic and analytical chemistry; and it is the hope of the authors that this series of experiments will not only be of assistance to teachers of theoretical chemistry, but will also serve in some degree to hasten and facilitate the introduction of instruction in the principles of chemical equilibrium and of electrolytic dissociation into the elementary courses.

A few lecture experiments of a somewhat similar character have been previously published. Those of Küster,<sup>2</sup> and of Lash Miller and Kenrick,<sup>3</sup> may be specially referred to.

The experiments are presented below in the form believed to be most convenient for those desiring actually to perform them. They are described in great detail, with the hope of saving others the large amount of time which has been expended in the attempt to find the best conditions for rapid and effective lecture demonstrations. It is, nevertheless, true that a slight accidental variation in one of the conditions, such as the dimensions of the apparatus employed, the temperature, or the concentration of the substances, may make modifications necessary; it is, therefore, of course, advisable to try the experiments before the lecture.

<sup>1</sup> Many of these experiments were shown in a lecture on "Some Applications of the Electrolytic Dissociation Theory" given before the American Chemical Society at its Columbus Meeting.

<sup>2</sup> *Ztschr. Electrochem.*, 4, 105.

<sup>3</sup> This Journal, 22, 291-300; See also Jones and Allen: *Am. Chem. J.*, 18, 377; and Stieglitz: *Ibid.*, 23, 404.

The principles illustrated have been stated as briefly as possible in a non-mathematical form: in spite of the familiarity of these principles, it has seemed desirable to state them explicitly, in order to make clear the exact significance of each experiment.

## PART I.—ELECTROLYTIC DISSOCIATION.

### EXPERIMENT I.

*Principle Illustrated.*—The physical properties of dilute aqueous salt solutions are additive, being dependent on the nature of the metal and of the acid component of the salt, but not on their mutual relations. Since most salts in moderately dilute aqueous solution are, according to the dissociation theory, almost completely dissociated into their ions, all properties of such solutions must be the resultant of the properties of the solvent and of the separate ions, each ion having a definite influence which is independent of the nature of the other ion simultaneously present and of that of the undissociated salt from which it originated. This principle is best illustrated in the case where one of the ions has a characteristic property, such as color, not possessed at all by the other ion. Thus, all the salts of a metal whose ion is colored must have the same color in dilute aqueous solution, provided the negative ion of the salt is colorless, however different may be the colors of the undissociated salts. The colors of the latter may be shown, either in the solid state, or in a concentrated alcoholic solution.

*Preparation of the Experiment.*—Dissolve 60 grams of powdered  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and 73 grams of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  each in 100 cc. of alcohol, thus making a fivefold normal solution of each salt. Dissolve 27 grams of anhydrous cupric chloride (made by heating the blue crystals in a porcelain dish over a free flame) and 48 grams of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , each in 100 cc. of absolute alcohol, thus making a fourfold normal solution of each salt. Pass into the cupric chloride solution a few cubic centimeters of dry hydrochloric acid gas. Place 20 cc. of each of these solutions in four large test-tubes. Provide also distilled water, concentrated ammonia, and 20 cc. of concentrated potassium cyanide solution.

*Experiment.*—Add 100 cc. of cold water to each of the four solutions. Then add 20 cc. of ammonia to one of the copper

solutions, and 20 cc. of concentrated potassium cyanide solution to one of the cobalt solutions.

*Observations.*—The alcoholic solutions of cobalt chloride and nitrate are deep violet-blue and purplish red, respectively, but become of the same shade of pink after dilution with water. Those of copper chloride and nitrate are originally greenish black and light blue, respectively, but become of the same shade of blue on dilution. The ammonia added to the copper solution produces a much more intense blue coloration of a different shade, and the potassium cyanide added to the cobalt solution changes its color from pink to brown.

*Remarks.*—The hydrochloric acid gas is passed into the cupric chloride solution in order to avoid the precipitation of a basic salt on subsequent dilution.

The change in color accompanying the dilution may well be due mainly to hydration of the salts rather than to dissociation of them; but whatever the cause, the experiment evidently still illustrates the principle of the dependence of the properties of dilute aqueous solutions on those of the separate ions. The addition of ammonia to the copper solution transforms the copper ions into complex positive ions of the form  $\text{Cu}(\text{NH}_3)_x$ ; and that of potassium cyanide to the cobalt solution converts the cobalt ions into complex negative ions, probably of the composition,  $\text{Co}(\text{CN})_6$ . These explanations show that the exceptions to the principle of additivity which are illustrated by the last part of the experiment are in full accord with the dissociation theory; for the nature of the ions having changed, the color of the solution must change likewise.

#### EXPERIMENT II.

*Principle Illustrated.*—Metathetical reactions between dissolved salts take place instantaneously, whatever may be the nature of the salts, while those in which organic compounds are involved commonly require an appreciable time which varies greatly with the nature of the compound. This difference of behavior is, according to the dissociation theory, due to the fact that the ions of salts, being already separated by the solvent, are capable of immediate combination, when those which have the tendency to combine are brought into contact, while the component elements

or radicals of organic substances must be separated from each other before they can enter into a metathesis. A very slight degree of dissociation of the salts is sufficient, however, owing to the fact that the ions removed by the metathesis are immediately replaced by others by the spontaneous and almost instantaneous process of dissociation.

*Preparation.*—Prepare 100 cc. of nearly saturated solution of potassium bromide and of zinc bromide in alcohol, and equal quantities of 5 per cent. solutions of isopropyl bromide, ethyl bromide, and phenyl bromide. Place these solutions in five lecture jars. Prepare 150 cc. of a nearly saturated alcoholic solution of silver nitrate (about 25 grams to the liter). Provide a stirring rod with one end flattened at right angles to the rod, for vertical stirring.

*Experiment.*—Add 20 cc. of the alcoholic silver nitrate solution to each of the five bromide solutions and stir.

*Observations.*—The potassium and zinc bromide solutions both give instantly with the silver nitrate a copious flocculent precipitate. The isopropyl bromide solution becomes turbid immediately, but an appreciable time is seen to be required for the completion of the precipitation. The ethyl bromide remains clear for a few seconds, and then becomes turbid, but the turbidity increases very slowly on standing. The phenyl bromide gives no turbidity, even after long standing.

*Remarks.*—Care must be taken that the ethyl and phenyl bromides are free from hydrobromic acid and bromine. These impurities, if present, may be removed by washing in a separatory funnel, first with dilute sodium carbonate solution, and then with water.

#### EXPERIMENT III.

*Principle Illustrated.*—The passage of electricity through a salt solution causes the metallic component of the salt to move in the direction of the current, and the acid component to move in the opposite direction. The products into which salts in aqueous solution are dissociated are therefore electrically charged molecules or ions.

*Preparation.*—Cut 10 grams of agar-agar in small pieces, place in a casserole, add 500 cc. of cold water, heat to boiling,

and boil until a clear solution is formed. Strain while still hot through a piece of cloth, and preserve the jelly formed on cooling as a stock for use in this and the next two experiments. To 35 cc. of the remelted agar add 8 cc. of saturated cupric chloride solution, a few drops of acetic acid, and 6 cc. of saturated potassium bichromate solution. Pour enough of this solution into a U-tube 2 cm. in diameter and 16 cm. high to fill the tube 3-4 cm. above the bend, and allow the jelly to harden. Sprinkle on each surface a little bone-black to mark the boundary, then pour into each arm a few drops (to fix the bone-black in place) of a solution made by mixing 4 cc. of saturated potassium chloride solution with 15 cc. of the melted stock-agar, cool in water, and after a few moments pour in enough more of this mixture to form a layer a few centimeters high in each arm. After this has hardened, pour into each arm a few cubic centimeters of saturated potassium chloride solution, insert electrodes of platinum wire in both arms, and connect them through an open switch and a 32 candle-power 110-volt lamp with the terminals of a 110-volt direct-current circuit. Place the U-tube in a beaker of water containing a large quantity of ice.

*Experiment.*—Close the switch and allow the current to pass through the tube for ten to thirty minutes, stopping it temporarily if the agar should show signs of melting.

*Observations.*—The copper chromate jelly filling the bottom of the tube has a deep green color. After the current has passed for some minutes a blue zone (due to the copper ions) appears above the bone-black boundary in one arm, and a yellow zone (due to chromate ions) above the bone-black in the other arm, and these zones both extend upwards as the electrolysis continues. The zones immediately below the bone-black in both arms also acquire a blue and yellow color respectively, while the central portion beneath remains unchanged in color.

*Remarks.*—The experiment should be prepared not more than an hour or two before the lecture, as otherwise the boundaries will not be sharp, owing to diffusion. It is desirable to use, as directed, a larger proportion of copper salt than corresponds to the normal chromate, since otherwise the color of the blue copper zone will not be deep enough to be visible at a distance. The



acetic acid is added to prevent the precipitation of a basic chromate. The potassium chloride in the arms of the tube serves to form a colorless conducting layer, its ions carrying the current to and from the boundary of the copper chromate. Accurate experiments have shown that the addition of enough agar to form a solid jelly does not affect the rate of migration of the ions more than a few per cent.; there is, therefore, no objection to its use for purposes of demonstration.

#### EXPERIMENT IV.

*Principle Illustrated.*—The rate of migration of the ions is dependent on their nature. The hydrogen ion moves most rapidly, the hydroxyl ion about one-half as fast, and other inorganic ions from one-fourth to one-eighth as fast as the hydrogen ion. The rate of motion of the ions and the number of them present are the two factors determining the conductivity of a solution.

*Preparation.*—Fill the bend of a U-tube (2 cm. in diameter, and 16 cm. high) and one of its arms up to a point 5 cm. from the top with a jelly made of 16 cc. of saturated potassium chloride solution, 12 drops of phenolphthalein solution, 50 cc. of the stock-agar (see Expt. III), and just enough potassium hydroxide to color it deeply red. Fill the other arm of the tube up to 5 cm. from the top with some of the same jelly to which has been added just twice as much hydrochloric acid as is needed to decolorize it. Place platinum wires in the air spaces at the top of each arm, and connect these wires through a 32-candle-power 110-volt lamp with the terminals of a 110-volt direct-current circuit in such a manner that the current will enter the arm containing the colored jelly. Place the tube in a beaker of water containing pieces of ice. Prepare a mixture of 0.5 cc. of hydrochloric acid (sp. gr. 1.12), 6 cc. of saturated copper chloride, and 20 cc. of water, and a mixture of 2 cc. of 10 per cent. potassium hydroxide solution with 20 cc. of saturated potassium chloride solution.

*Experiment.*—Nearly fill the arm of the tube containing the colored jelly with the solution of copper chloride and hydrochloric acid and the other arm with the solution of potassium hydroxide

and chloride, close the switch, and allow the current (of about 0.5 ampere) to pass for about fifteen minutes.

*Observations.*—A colorless zone (due to the hydrogen ions) descends into the pink jelly to a depth of about  $5\frac{1}{2}$  cm., and this is followed by a blue zone (due to the copper ions) to a depth of 1 cm. In the other arm a pink zone (due to the hydroxyl ions) descends into the colorless jelly to a depth of about  $2\frac{1}{2}$  cm.

#### EXPERIMENT V.

*Principle Illustrated.*—The composition of the ions can be determined by migration experiments. Thus in the case of the double cyanide of potassium and silver, the silver can be shown to move against the current, thus proving that it forms a part of the negative ion, which has in fact been shown to have the composition  $\text{Ag}(\text{CN})_2$ .

*Preparation.*—Charge a U-tube, 2 cm. in diameter and 16 cm. high, not more than an hour or two before the experiment is to be performed, in the manner shown in the accompanying scale drawing, with various jellies, designated I, II, III, and IV. Jelly No. I, is prepared from 30 cc. of the stock-agar (Expt. No. III), 6 cc. of saturated potassium nitrate solution, and 6 cc. of a suspension of washed precipitated zinc sulphide in water; jelly No. II, from 15 cc. of the agar and 4 cc. of saturated potassium nitrate solution; jelly No. III, from 5 cc. of the agar, 1 cc. of saturated potassium nitrate, and 1 cc. of a 3 per cent. silver nitrate solution; and jelly No. IV, from 5 cc. of the agar, 1 cc. of saturated potassium nitrate solution, and 1 cc. of a potassium silver cyanide solution made by adding concentrated potassium cyanide solution, drop by drop, to a 3 per cent.

Fig. 1.

silver nitrate solution until the precipitate first formed redissolves. In charging the tube, pour in each portion of melted jelly through a long-necked funnel to avoid contaminating succeeding portions, and cause each to harden by immersing in cold water before adding the next. Make each of the layers of a thickness corresponding to that shown in the drawing, taking especial care that the layers

of jelly II be not more than 1 cm. thick, since otherwise too long a time will be required for the experiment; and in forming the last layers, pour in first a few drops of the solution, allow this to solidify, and then add the remainder, in order to prevent them from taking up and mixing with any of the jelly beneath. Pour into each arm on top of the jelly some saturated potassium nitrate solution, insert platinum wires, and connect them with the terminals of a 110-volt direct-current circuit in such a manner that the current will enter the arm containing the silver nitrate jelly (No. III). Immerse the tube in a beaker of ice and water.

*Experiment.*—Cause the current (which will be one of about 0.35 ampere) to pass through the tube for fifteen to twenty minutes, stopping it temporarily or inserting additional resistance if the agar shows signs of melting.

*Observations.*—The zinc sulphide jelly at the bottom, which is pure white at first, after a few minutes begins to blacken at its surface below the silver nitrate, and a few minutes later at its other surface below the potassium silver cyanide, the blackening extending rapidly downward on both sides. The zinc sulphide layers near the top of the arms remain white throughout the experiment.

*Remark.*—Zinc sulphide is used instead of an alkaline sulphide to indicate the presence of silver, since, being nearly insoluble, it does not move appreciably with the current.

#### EXPERIMENT VI.

*Principle Illustrated.*—The molecular conductivity of salts increases on dilution at first rapidly, and then more slowly, and finally attains a constant maximum value which is not affected by further dilution. The molecular conductivity of a dissolved substance is the conductivity of that volume of its solution which contains 1 mol. of the substance, when the solution is placed between parallel electrodes of sufficient extent, 1 cm. apart. According to the dissociation theory, the change of this property on dilution results from the fact that electricity is transported through the solution solely by the ions, and the number of these is increased at the expense of the undissociated portion of the salt by increased dilution, up to the point where the salt is com-

pletely dissociated, after which further dilution has, of course, no further effect.

*Preparation.*—Construct a high, narrow trough with parallel glass sides and wooden ends and base in the following manner: Cover one of the broad surfaces of each of two strips of wood 45 cm. long, 1 cm. thick, and 2.2 cm. wide, previously oiled and shellaced, with a strip of thin silver foil, attaching this to the wood by means of shellac. Insert these two strips of wood with the silver-covered surfaces towards each other and *uniformly* 18.5 cm. apart between two sheets of plate glass ( $45 \times 22.5 \times 0.6$  cm.) so as to leave a free space about 1 cm. deep outside of the strips. Clamp the apparatus together temporarily, and fill this free space with a melted cement made by stirring one part of beeswax into five parts of melted rosin. Bind tightly over each of these two ends a piece of stout cloth or canvas, and attach it to the glass sides by means of shellac, so as to hold the whole in position. Insert this cell into a wooden base so made that the cell will fit tightly into a groove to a depth of 1.5 cm.; pour on to the bottom inside more of the above cement heated enough to be very fluid, and allow the cement to cool, so as to form an even horizontal layer. Solder wires to the tops of the silver electrodes. Connect the resistance cell thus constructed in series with a storage cell, a switch, and a suitable current indicator. Use as a current-indicator any Weston station voltmeter, from which the series resistance coil in the back has been removed or short circuited. (The moving coils in all the Weston station voltmeters have a resistance of about 75 ohms; and a full scale deflection is obtained with a current of about 0.012 ampere; the station type is used since it has a pointer which can easily be seen at a distance.) Prepare a stirring rod by closing up one end of a wide glass tube 0.6 meter long. Provide a glass siphon suitable for emptying the resistance cell, and fill it with water; also a funnel attached to a tube long enough to reach the bottom of the cell. Measure out in four graduates three portions of distilled water of 60, 240, and 960 cc., respectively. Prepare 20 cc. of a fourfold normal silver nitrate solution by dissolving 13.5 grams of solid silver nitrate in water, and making the volume up to 20 cc.

*Experiment.*—Fill the resistance cell with distilled water, and close the switch for a few moments. Insert the siphon, and empty the cell completely, tilting it at the end. Then pour into the bottom of the cell through the funnel the 20 cc. of fourfold normal silver nitrate solution. Close the switch, and note on the board the scale reading. Then pour into the cell the 60 cc. portion of water, stir, and note the reading. Then pour in successively the 240 cc. and the 960 cc. portions of water, noting the readings after the complete addition of each portion.

*Observations.*—A scarcely noticeable deflection of the needle is produced when the cell is filled with pure water. The scale-readings corresponding to the most concentrated solution and the first fourfold dilution of it are found to differ greatly, those of the first and second dilutions much less, and those of the second and third dilutions by only a relatively small amount; thus the scale-readings in an actual experiment were 7.1, 8.4, 9.2, and 9.5.

*Remarks.*—In the apparatus and experiment above described the distance between the electrodes, though not 1 cm., is a constant distance, and the amount of the salt used, though not 1 mol, is a definite amount, so that a satisfactory illustration is given of the property of molecular conductivity and of its variation with the dilution, a phenomenon, which, as is well known, was the starting-point of the electrolytic dissociation theory, and one which forms the basis of the most important method of determining dissociation.

The molecular conductivities of the silver nitrate solutions are at the four concentrations, according to Kohlrausch, approximately 39, 63, 80, and 92 units. The effect of having the resistance (about 75 ohms) of the voltmeter constantly in series with the cell is to make the apparent change of conductivity less than the true change; nevertheless, the effect is sufficiently great to make the demonstration an entirely satisfactory one, as is shown by the scale-readings cited above.

If copper electrodes are substituted for the silver ones, and a copper salt solution for the silver nitrate, the change of conductivity with the dilution is still greater; but the experiment is far less satisfactory, for it is not possible, owing to the great dilu-

tion required, to illustrate the approach to a maximum value.

#### EXPERIMENT VII.

*Principle Illustrated.*—Different acids of the same concentration differ greatly in their conductivities and degrees of dissociation; but their neutral salts have approximately the same conductivities and same degrees of dissociation.

*Preparation.*—Fill four 500 cc. bottles with half-normal solutions of hydrochloric acid, sulphuric acid, chloracetic acid, and acetic acid, prepared by weighing out the calculated amounts of the commercial acids. (It is desirable, however, to prove the approximate equivalence in the concentrations of the four acids by titration with normal potassium hydroxide, and to adjust them if they differ by more than five per cent.) Distinctly label these solutions, and reserve them for use in this and later experiments.

Make the apparatus represented in the accompanying figure in the following manner: Procure four glass tubes as nearly alike as possible, of an internal diameter of about 3 cm. and a length of 20 cm. (The straight parts of "student lamp" chimneys can be used for the purpose.) Place in one end of each of these tubes a rubber stopper with one hole in which has been inserted a small glass tube containing a stout copper wire to which a thin circular platinum disk is soldered, this disk covering the small end of the rubber stopper and being attached to it by means of sealing-wax. Set up the tubes in a vertical position with the stoppers at the bottom, holding the tubes in place by means of clamps or by a suitable wooden frame made for the purpose. Insert in the upper end of each of the tubes a rubber stopper carrying a small thick-walled glass tube 22 cm. long through which passes a stout copper wire, to the lower end of which is soldered, at right angles to the wire, a thin circular platinum disk of a diameter a few millimeters less than that of the tube, the disk being reinforced by a thick layer of sealing-wax on its upper surface. These tubes should move freely through the stoppers, but yet be held in place by them. Connect the wire issuing from the bottom of each large tube with a 32-candle-power 110-volt lamp placed in a socket beneath; make also the other connections shown in the drawing, using short coils of

covered flexible wires between the four upper electrodes; and finally, connect through an open switch the upper electrodes with one terminal and the lamps with the other terminal of a

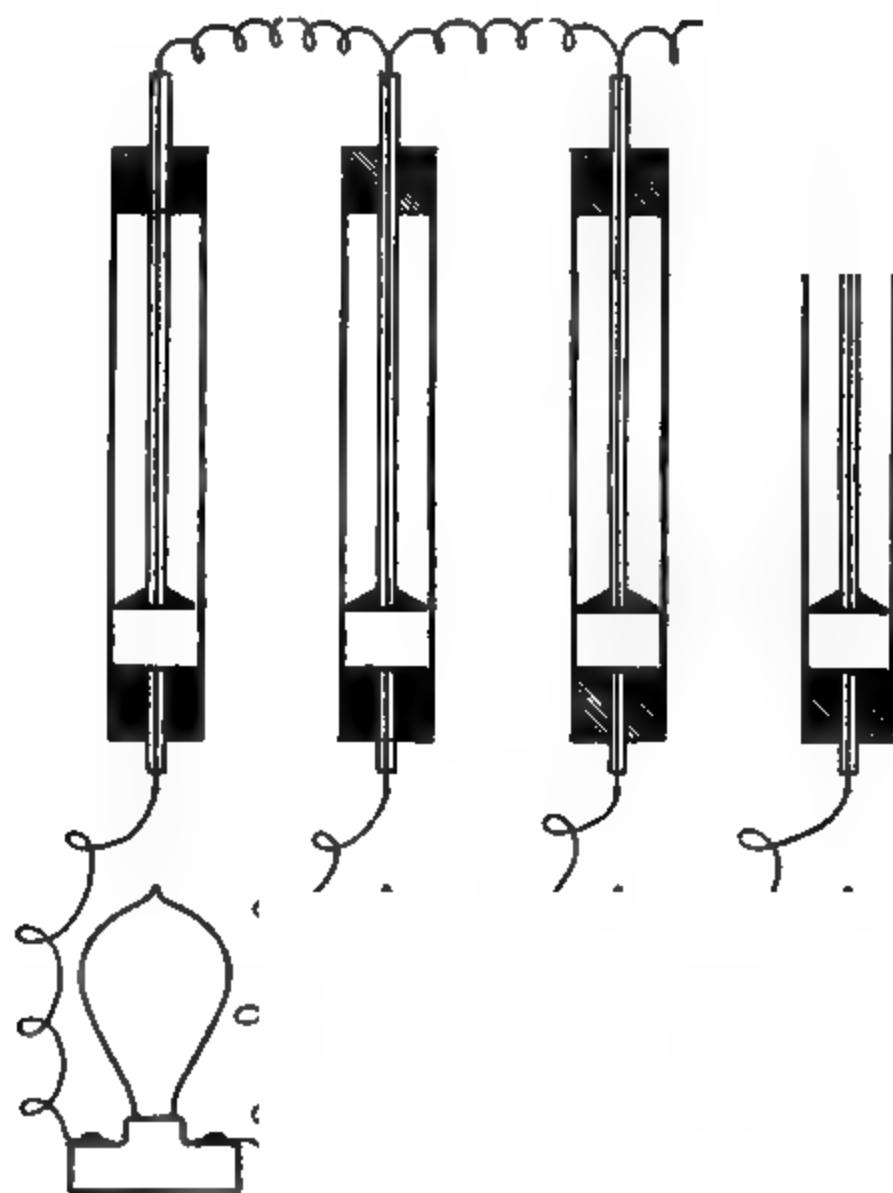


Fig. 2.

110-volt alternating circuit. Place in each tube 120 cc. of distilled water and set the electrodes one-third of the distance from the bottom. Provide a 5 cc. graduated pipette, a little phenolphthalein solution, and 50 cc. of normal potassium hydroxide solution.

*Experiment.*—Raise the stoppers carrying the upper electrodes, and add to each of the four tubes with the pipette 5 cc. of each of the four half-normal acids, so that they will be in the order, acetic, chloracetic, sulphuric, hydrochloric, and stir thoroughly. Re-insert the electrodes, darken the room somewhat, and close

the circuit. Raise the electrode in the hydrochloric acid solution to the top of the tube, and then adjust the heights of the other three electrodes so that all the lamps beneath glow with equal brilliancy. Admit the light to the room, and call attention to the relative heights of the four electrodes. Then raise the stoppers, and add to each tube two or three drops of phenolphthalein solution and from the pipette about 2.5 cc. of a normal solution of pure potassium hydroxide, adding the last few drops in each case slowly and with vigorous stirring, until the solution remains permanently colored. Again darken the room, set the electrode in the potassium chloride solution about one-third of the total distance from the bottom, and adjust the other three electrodes so that all four lamps glow with equal brilliancy. Admit the light to the room, and call attention to the heights of the four electrodes.

*Observations.*—Starting as directed with the four electrodes at the same height, about one-third of the distance from the bottom, it is seen when the circuit is closed that the lamps are more brilliant in correspondence with the order, hydrochloric, sulphuric, chloracetic, acetic, the lamp beneath the last-named acid not glowing perceptibly. After the lamps are brought to equal brilliancy by adjusting the electrodes, it is seen that if the upper electrode in the hydrochloric acid is at the top, that in the sulphuric acid is about one-fourth of the distance down, that in the chloracetic acid three-fourths of the distance down, and that in the acetic acid nearly touching the lower electrode. It is seen that nearly equal amounts of potassium hydroxide are required for the neutralization of all four acids, thus proving them of equal concentration. Finally after adjusting the lamps to constant brilliancy, the electrodes in the salt solutions are seen to stand at not far from the same heights.

*Remarks.*—The chloracetic acid solution must be prepared not more than a few days before it is used, since, otherwise, it will contain an appreciable amount of hydrochloric acid. If an alternating circuit is not available, a direct circuit may be used, but in that case it is desirable that the upper electrodes be made convex downwards so that the gas will escape, and that the circuit be closed only for as short a time as is necessary.



Instead of charging the tubes of the conductivity apparatus during the lecture with the acids, this may be done beforehand, in order to save time ; but in that case, the audience is obliged to take for granted the fact that the acids used in the later experiments are identical with those used in this one, a fact which is made obvious if the portions of acids are in each case drawn from the same bottles. In fact, throughout most of the following experiments, much time can be saved in the lecture by measuring out the solutions in advance, the audience being asked to accept the lecturer's statement in regard to their composition. While the purpose of such experiments is to illustrate rather than to demonstrate, it is nevertheless true that they become less satisfactory, the more the audience has to take for granted. To what extent it is desirable to carry the preparation of the experiments, will therefore depend on the character of the lectures, on the time that can be given to experiments, and whether the services of an assistant are available during the lecture.

Lecturers will, we believe, find themselves repaid for the small amount of labor involved in the construction of the apparatus just described; for not only is the above experiment a very satisfactory one, but the same apparatus can be employed for the demonstration of Ostwald's dilution law (see Expt. XII), and for the illustration of the conductivity and dissociation of many substances besides those here used. It should be stated that the apparatus was devised and first constructed by Dr. W. R. Whitney of our Institute.

## PART II.—THE VELOCITY OF CHEMICAL REACTIONS.

### EXPERIMENT VIII.

*Principle Illustrated.*—The rate at which a chemical change takes place is proportional to the concentration of each of the substances taking part in it.<sup>1</sup>

*Preparation.*—In a 2-liter bottle put 1600 cc. of distilled water, 50 cc. of half-normal hydrochloric acid, and 40 cc. of starch solution (made by rubbing 1 gram of potato starch to a paste with

<sup>1</sup> As is well known, the rate is in some cases proportional to that power of the concentration which corresponds to the number of molecules involved ; but this experiment illustrates only the simpler case.

5 cc. of cold water, pouring 150 cc. of boiling water over it, allowing the undissolved part to settle, and decanting the supernatant liquid). Prepare a 0.5 normal solution of potassium bromate by dissolving 7 grams of the salt in half a liter of water; also a 0.5 normal solution of potassium iodide by dissolving 42 grams of it in half a liter of water. Reserve these solutions for use in the three following experiments: Provide four 500 cc. white glass stoppered bottles, 8 cm. in diameter, and set two 10 cc. graduates in front of each of them. Prepare a standard blue solution in a fifth 500 cc. bottle by adding to 400 cc. of water, 10 cc. of the starch solution and 1 cc. of a solution of 1 gram of iodine and 2 grams of potassium iodide in 500 cc. of water. Place all five bottles on the lecture table against a background of white paper. Provide a large clock (or stop-watch) with a second hand; also a 500 cc. graduate.

*Experiment.*—Pour into each of the four bottles from the large graduate 400 cc. of the acid solution in the 2-liter bottle. Pour into the four pairs of 10 cc. graduates respectively 5 cc. of the bromate and 5 cc. of the iodide solution, 10 cc. bromate and 5 cc. iodide, 5 cc. bromate and 10 cc. iodide, and 10 cc. bromate and 10 cc. iodide. Add to each of the four bottles the bromate solution from the graduate before it, and then, at a definite instant, when the second hand of the clock shows an even minute, add simultaneously to the four bottles the measured portions of iodide solution, quickly insert the stoppers, and shake vigorously. Note on the board by reference to the clock the times when each of the solutions becomes of the same shade of blue as the standard, placing the latter in succession by the side of the different reaction bottles.

*Observations.*—The mixture containing the 10 cc. of both bromate and iodide will become of the same shade of blue as the standard in about thirty seconds. The mixtures with 10 cc. bromate and 5 cc. iodide and with 5 cc. bromate and 10 cc. iodide will both require the same interval of time, which will be about twice as great as that for the first mixture. The mixture containing 5 cc. of both bromate and iodide will require nearly twice as much time as these last mixtures.

## EXPERIMENT IX.

*Principle Illustrated.*—Equal increments of temperature cause an equal multiplication of the velocity of any definite chemical reaction.<sup>1</sup>

*Preparation.*—Mix in a 2-liter bottle 1100 cc. of water, 100 cc. of 0.5 normal hydrochloric acid, and 30 cc. of starch solution. Put 400 cc. of this solution into each of three 500 cc. white glass-stoppered bottles (8 cm. in diameter) ; bring by means of suitable baths one of these solutions to 4°, another to 16°, and the third to 28° ; and allow the bottles to stand in the baths until the experiment is to be shown. Mix in a 50 cc. graduate 10 cc. of 0.5 normal potassium bromate, 10 cc. of 0.5 normal potassium iodide, and 25 cc. of water, all measured as closely as possible ; and pour just 10 cc. of this mixture into each of three 10 cc. graduates. Provide a clock with a second hand, and a large thermometer of short range whose readings are visible at a distance. Prepare in a fourth bottle, just as in Expt. VIII, a blue iodide of starch solution to serve as a standard. Place all four bottles against a background of white paper.

*Experiment.*—Insert the thermometer in succession in each of the three bottles, and note the temperatures on the board. At a definite instant, when the clock shows an even minute or half minute, pour the three portions of bromate solution into the three bottles, stopper quickly, and shake vigorously. Note on the board the times at which the three solutions reach the same depth of blue as the standard.

*Observations.*—The times required to reach the color of the standard will be about thirty-two seconds, fifty-eight seconds, and one hundred and five seconds at 28°, 16°, and 4°, respectively.

*Remarks.*—The hottest solution must not be above 30°, since otherwise a considerable error arises from the lessening of the depth of color of the iodide of starch. Between 4° and 30°, however, the intensity of color undergoes a scarcely perceptible change, as was proved by a special experiment.

## EXPERIMENT X.

*Principle Illustrated.*—The effect of acids in accelerating chem-

<sup>1</sup> This principle may be somewhat more explicitly stated as follows : In the case of any chemical reaction, the velocity-coefficients corresponding to an arithmetical series of temperatures, form a geometrical series.

ical reactions is roughly proportional to their electrical conductivities. The effect is primarily dependent on the hydrogen ions, and is in most cases approximately proportional to their concentration.<sup>1</sup>

*Preparation.*—Mix in a 2 liter bottle, 40 cc. of 0.5 normal potassium iodide, 40 cc. of 0.5 normal potassium bromate, 40 cc. of starch solution, and 1600 cc. of water. Place on the lecture table the four half-normal solutions used in Expt. VII, four 500 cc. bottles, four 10 cc. graduates, a 500 cc. graduate, and white paper arranged so as to serve as a background.

*Experiment.*—Measure with the large graduate 400 cc. of the bromate-iodide mixture into each of the four bottles. Pour into the small graduates just 10 cc. of each of the half-normal acids, and place them in front of the four bottles in the order hydrochloric, sulphuric, chloracetic, acetic acid. Add at the same instant the contents of the four graduates to the bottles, stopper quickly, and shake.

*Observations.*—The solution containing the hydrochloric acid becomes deep blue almost immediately; that with the sulphuric acid, within half a minute; that with the chloracetic acid, after three or four minutes; and that with acetic acid, only after three or four hours.

#### EXPERIMENT XI.

*Principle Illustrated.*—Neutral substances sometimes act as powerful catalytic agents.

*Preparation.*—Place in a liter bottle 800 cc. of water, 40 cc. of 0.5 normal potassium iodide, 40 cc. of 0.5 normal potassium bromate, and 20 cc. of starch solution. Provide a half-normal solution of acetic acid and a neutral saturated solution of ferrous sulphate; also, a graduated 1 cc. pipette, two 500 cc. bottles, and two 50 cc. and one 500 cc. graduates.

*Experiment.*—Measure into each of the two bottles, with the large graduate, 400 cc. of the bromate-iodide mixture. Measure out in each of the two graduates 50 cc. of the half-normal acetic acid, and add to one of the graduates 0.5 cc. of the ferrous sul-

<sup>1</sup> In the case of the bromate-iodide reaction the accelerating effect increases much more rapidly than the concentration of the hydrogen ions (see *Ztschr. phys. Chem.*, 24, 599); but in spite of this exceptional behavior, it can be used to demonstrate the order of the effect of different acids, which is all that is attempted in this experiment.

phate solution. At the same moment add the contents of the graduates to the two bottles, quickly insert the stoppers, and shake.

*Observations.*—The solution containing the ferrous sulphate becomes deep blue within a few seconds, while that not containing it requires as many minutes to reach the same depth of color.

### PART III.—CHEMICAL EQUILIBRIUM OF DISSOCIATED SUBSTANCES.

#### EXPERIMENT XII.

*Principle Illustrated.*—The molecular conductivity, and therefore the dissociation, of a slightly dissociated acid varies as the square root of the volume in which a definite quantity of the acid is contained, in accordance with the requirement of the mass action law. The general expression of the effect of dilution on the dissociation of acids, or of the so-called Ostwald's dilution law, is

$$\frac{d^2}{(1-d)v} = K,$$
 where  $d$  is the degree of dissociation,  $v$  the volume containing 1 molecule, and  $K$  the dissociation-constant. If  $d$  is small, the quantity  $(1-d)$  can be considered equal to unity without great error, whence the above-stated principle follows.

*Preparation.*—Place on the lecture table the conductivity apparatus and the half-normal chloracetic acid solution used in Expt. VII. Provide two 300 cc. beakers and a 50 cc. and a 200 cc. graduate, also half a liter of distilled water and have this at the same temperature (that of the room) as the chloracetic acid. Connect the conductivity apparatus through a switch with the terminals of a 110-volt alternating circuit.

*Experiment.*—Mix in a beaker 50 cc. of the half-normal chloracetic acid solution with 150 cc. of water. In a second beaker dilute 50 cc. of the solution so obtained with 150 cc. of water. Nearly fill three of the tubes of the conductivity apparatus with the half-normal chloracetic acid from the bottle, and with the two diluted solutions in the beakers, respectively. Raise the electrode in the tube containing the most concentrated acid to the top, darken the room, close the circuit, and adjust the other two electrodes so that the three lamps beneath glow with equal brilliancy.

Open the circuit, admit the light, and call attention to the position of the electrodes.

*Observations.*—At the close of the experiment it is seen that the electrodes in the half-normal solution are about twice as far apart as those in the eighth-normal solution, and about four times as far apart as those in the  $1/32$ -normal.

*Remarks.*—The remark on Expt. VII in regard to the use of a direct current applies here also.

The distances between the electrodes are directly proportional to the specific conductivities of the solutions; consequently, the molecular conductivities are proportional to the products of these distances into the volumes in which a definite amount of acid is contained.

Chloracetic acid is 5.4, 10.5, and 20.0 per cent. dissociated in  $1/2$ ,  $1/8$ , and  $1/32$ -normal solutions respectively. Owing to the rather large degree of dissociation, the proportionality between this and the square root of the volume is not exact; but the deviations are not great enough to be noticeable in the experiment here described.

#### EXPERIMENT XIII.

*Principle Illustrated.*—The dissociation of a slightly dissociated acid (or base) is very greatly reduced by the addition of an equivalent quantity of one of its neutral salts. For, according to the mass action law, the product of the concentrations of the two ions of the acid is proportional to the concentration of its undissociated portion, and since the concentration of the negative ion is largely increased by the addition of the neutral salt, the ratio of the concentration of the hydrogen ion to that of the undissociated acid must decrease in the same proportion. In the following experiment, in order to show the difference in the concentrations of the hydrogen ion in the two cases, use is made of the relative effects of the acid, in the absence and presence of its neutral salt, in accelerating the bromate-iodide reaction.

*Preparation.*—In a liter bottle place 700 cc. of distilled water, 20 cc. of 0.5-normal potassium bromate, 20 cc. of 0.5-normal potassium iodide, and 10 cc. of starch solution. Place on the lecture table the half-normal solution of chloracetic acid and a normal one of potassium hydroxide; also a 500 cc. graduate,

two 100 cc. graduates, a 200 cc. beaker, two 500 cc. bottles, a phenolphthalein solution, and some distilled water.

*Experiment.*—Measure with the large graduate, 350 cc. of the bromate-iodide mixture into each of the 500 cc. bottles. Measure out 40 cc. of chloracetic acid into each of the two 100 cc. graduates. To one graduate add 60 cc. of water, and mix by stoppering the graduate and shaking. Pour the contents of the other graduate into the beaker, add a few drops of phenolphthalein and about 20 cc. of the normal potassium hydroxide solution, adding the last portion slowly with stirring so as to attain closely the neutral point; then add 40 cc. more of the chloracetic acid solution and pour the mixture back into the graduate. At the same moment add the contents of the two graduates to the two bottles containing the bromate-iodide mixture, insert the stoppers, and shake vigorously.

*Observations.*—The blue color appears very quickly in the bottle to which only the chloracetic acid was added, but much more slowly in that containing also the neutral salt.

*Remark.*—The same principle is further illustrated in connection with the two following experiments.

#### EXPERIMENT XIV.

*Principle Illustrated.*—The extent to which a weak acid is displaced from one of its neutral salts by another acid added to its solution increases with the degree of dissociation of the added acid. For the displacement depends on the fact that the negative ions of the salt and the hydrogen ions of the added acid when brought together unite in part to form undissociated acid, and the quantity of this which forms is, according to the mass action law, greater, the greater the concentration of the hydrogen ions and therefore the greater the dissociation of the added acid.

*Preparation.*—Dissolve 6 grams of commercial crystallized alloxan and 2 grams of hydroxylamine hydrochlorate in 200 cc. of water, heat for an hour on a water-bath, and exactly neutralize the solution of violuric acid so prepared with dilute potassium hydroxide solution, with the help of litmus paper, rinsing off the pieces of paper with water after their immersion in the solution, so as to make the color of the litmus evident. (About

55 cc. of a normal solution are required.) Dilute with enough water to make the volume 450 cc. Measure six 50 cc. portions of this solution into six lecture test-tubes 3 cm. in diameter, placed in a rack provided with a background of white paper. Determine accurately the amount of half-normal hydrochloric acid which suffices to decolorize one of these portions to such an extent that it appears of a pale, but distinctly recognizable, pink shade. (Roughly 6 cc. will be required. The exact quantity required is designated M cc. below.) Then entirely decolorize this portion by adding a few more drops of acid. Provide a 10 cc. graduated pipette, an additional lecture test-tube, the four half-normal acid solutions used in Expt. VII, a normal potassium hydroxide solution, a phenolphthalein solution, and a 10 cc. graduate containing a chloracetate solution made by nearly but not quite neutralizing M cc. of the half-normal chloracetic acid with normal potassium hydroxide and diluting up to 10 cc.

*Experiment.*—Add potassium hydroxide solution in excess to the colorless violuric acid solution, and remove the tube from the rack. Add by means of the 10 cc. graduated pipette to one of the tubes of sodium violurate M cc. of water to serve as a standard and to the four other tubes M cc. of the four half-normal acids in the order acetic, chloracetic, sulphuric, and hydrochloric. Pour one-half of the portion to which the chloracetic acid has been added into the empty test-tube; and add to this 10 cc. of water; and to the half in the original tube add the 10 cc. of chloracetate solution previously prepared after adding to the latter a drop of phenolphthalein solution (to show that it is not alkaline).

*Observations.*—The colorless violuric acid solution becomes a deep violet when the potassium hydroxide is added. The acetic acid reduces the color to about one-half, and the chloracetic acid to about one-tenth that of the standard; the sulphuric acid gives rise to a pale pink, which, however, is considerably deeper than that produced by the hydrochloric acid. The color of the portion to which both the chloracetic acid and the chloracetate are added is about twice as intense as that of the portion which contains only the chloracetic acid.

*Remarks.*—The purpose of the addition of potassium hy-



droxide at the start is to illustrate the facts on which the demonstration of the main principle depends, namely that violuric acid in solution is nearly colorless and that its salt is of a deep violet color. The last part of the experiment on the effect of the neutral salt is a further illustration of the principle here under consideration as well as of that underlying Expt. XIII.

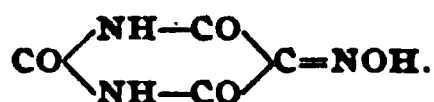
Violuric acid<sup>1</sup> is an acid of about the same strength as acetic acid, the dissociation constants of the two acids being 0.0027<sup>2</sup> and 0.0018, respectively; consequently, the base divides itself nearly equally between the two acids when, as in the experiment, equivalent quantities of them are simultaneously present. Violuric acid is so very much weaker than sulphuric and hydrochloric acids that it is almost completely displaced by both of them; and, to make evident a difference in their behavior, it is necessary to avoid adding enough hydrochloric acid to cause complete decolorization, and to measure quite accurately the amounts of the two acids added; for 10 per cent. excess of the sulphuric acid entirely obscures the difference in their behavior.

#### EXPERIMENT XV.

*Principle Illustrated.*—The behavior of indicators used in titrating acids and alkalies is primarily determined by the principles governing the displacement of one acid (or base) from its salt by another. It depends on the relative degree of dissociation of the indicator, which must itself be a very slightly dissociated acid or base, and of the titrated acid (or base.) The behavior of indicators is in some cases also greatly influenced by the phenomenon of hydrolysis. The behavior of di- and tri-basic acids is dependent on the different degrees of dissociation of the acid with respect to its first and second, or first, second, and third hydrogen atoms. More specific explanations follow the experiments described below.

*Preparation.*—Place 250 cc. of distilled water in each of ten lecture jars of 400 cc. capacity. Provide the following apparatus and solutions: four 50 cc. graduates; several stirring rods with one end flattened at right angles to the rod; two pipettes with rubber

<sup>1</sup> The constitutional formula of the acid is



<sup>2</sup> Magnanini: *Ztschr. phys. Chem.*, 12, 58.

nipples for dropping; half-normal solutions of hydrochloric acid and acetic acid, and normal solutions of potassium hydroxide, ammonium hydroxide, sodium acetate, sodium carbonate, and phosphoric acid (made by diluting 12 cc. of sirupy phosphoric acid of 1.34 specific gravity up to 500 cc.); and solutions of phenolphthalein and methyl orange as ordinarily prepared for volumetric analysis.

*Experiment.*—1. Add from the dropping pipette, to each of four of the lecture jars containing water 3 drops of the normal potassium hydroxide solution. To the first and third of these jars add five drops of phenolphthalein and to the second and fourth add five drops of methyl orange. Then add from the pipette, drop by drop, half-normal hydrochloric acid to the first and second jars, and half-normal acetic acid to the third and fourth jars with constant stirring, until the indicator becomes decolorized or changes color. In the case of the fourth jar, after showing that the first few drops cause no change in color, add the acetic acid in larger quantities from a graduate until about 40 cc. have been added. Then add 25 cc. of normal sodium acetate to both the third and fourth jars.

2. To the fifth jar add just 50 cc. of half-normal hydrochloric acid and five drops of methyl orange. To the sixth jar add the same amount of the hydrochloric acid and two drops of phenolphthalein. Add to each jar from a 50 cc. graduate normal ammonium hydroxide, rapidly until 23–24 cc. are added, and then more slowly until the (sharp) end-point is reached in the fifth jar when about 25 cc. have been added, and until the solution becomes of a decided red color in the sixth jar, requiring about 40 cc. Then add ten drops more of phenolphthalein to the latter.

3. Add to the seventh and eighth jars 25 cc. of normal sodium carbonate, and to the former, five drops of methyl orange, and to the latter, five drops of phenolphthalein. Titrate roughly to an end-point with normal hydrochloric acid, adding from a graduate about 50 cc. to the seventh jar and 25 cc. to the eighth.

4. Add to the ninth and tenth jars 50 cc. of normal phosphoric acid and to the former jar five drops of methyl orange and to the latter five drops of phenolphthalein. Titrate roughly to an end-

point with normal potassium hydroxide, adding from a graduate about 17 cc. to the ninth jar and about 34 cc. to the tenth.

*Observations and Explanations.*—1. The end-point is sharp and requires for its attainment the same quantity of acid whether hydrochloric acid with phenolphthalein, hydrochloric acid with methyl orange, or acetic acid with phenolphthalein, is used; but when acetic acid and methyl orange are employed, the change of color is very gradual and requires a much larger quantity of acid. These results are explained as follows: hydrochloric acid is so much stronger (*i. e.*, more dissociated) than either phenolphthalein or methyl orange, and acetic acid is so much stronger than phenolphthalein, that the indicator is completely displaced from its potassium salt by even an inappreciable excess of the acid; on the other hand, since methyl orange is a relatively strong indicator-acid<sup>1</sup> and acetic acid a relatively weak acid, a large excess of the latter, whereby a considerable concentration of the hydrogen ions results, is necessary in order to displace the indicator completely from its salt. The sodium acetate added at the close of this experiment causes the yellow color of the methyl orange salt to reappear, owing to the great reduction of the dissociation of the acetic acid, whereby it loses its power of displacing the indicator from its salt; this reduction by the sodium acetate is, however, not sufficient to cause any apparent change in the phenolphthalein equilibrium.

2. In titrating hydrochloric acid with ammonium hydroxide, the end-point is sharp when methyl orange is used, while the change to a pink color is very gradual when phenolphthalein is employed. The remarkable behavior of this last indicator is due to the fact that it is such a very weak acid that when the base also is weak, as is the case with ammonium hydroxide, the salt resulting from their union is so readily decomposed by water that an appreciable quantity of it does not form until the ammonium hydroxide is present in considerable excess; on the other hand, methyl orange is so strong an acid that its salts even with weak bases like ammonium hydroxide are not much hydrolyzed. The addition of more phenolphthalein at the end of the exper-

<sup>1</sup> Other hypotheses in regard to the behavior of this indicator have been proposed by Küster (*Ztschr. anorg. Chem.*, 13, 136) and Waddell (*J. Phys. Chem.*, 2, 171); but these lack experimental verification.

iment intensifies the red color; for it causes, just as the excess of ammonium hydroxide does, a decrease in the amount of hydrolysis.

3. The results observed in this experiment are indicated in the description of it. They are explained as follows: the acid ion  $\text{HCO}_3$ , which begins to form on the first addition of hydrochloric acid, is less dissociated than either of the two indicator acids and consequently does not displace either of them from its salts. When a little more than one equivalent of acid has been added, however, the acid  $\text{H}_2\text{CO}_3$  begins to form, and since its dissociation is greater than that of phenolphthalein but less than that of methyl orange, it displaces the former, giving an end-point, but does not displace the latter.

4. The results are indicated above. They are readily explained with the help of the following assumptions: The acid  $\text{H}_3\text{PO}_4$  is a stronger acid than either of the indicators; the ion  $\text{H}_2\text{PO}_4$  is a stronger acid than phenolphthalein, but a weaker one than methyl orange; and the ion  $\text{HPO}_4$  is a weaker acid than either of the two indicators.

#### EXPERIMENT XVI.

*Principle Illustrated.*—The product of the concentrations of the ions of a salt with which a solution is saturated (the so-called solubility-product) has the same value whether or not other substances are simultaneously present. The presence of a second salt with a common ion therefore reduces the solubility in accordance with this principle; and two different salts, one having in common the positive ion and the other the negative ion of the salt saturating the solution, must have the same effect in reducing the solubility, assuming, as is usually approximately true, that the two salts are equally dissociated.

*Preparation of the Experiment.*—Prepare 500 cc. of a saturated solution of silver acetate by shaking an excess of the solid salt with warm water, cooling, and filtering or decanting. Place 200 cc. of this solution in each of two 400 cc. lecture jars. Place in graduates 5 cc. of fourfold normal solutions of sodium acetate and of silver nitrate; also provide a stirring rod.

*Experiment.*—Add the measured portion of sodium acetate to

one jar and that of silver nitrate to the other jar of the silver acetate solution, and stir vigorously for a few moments.

*Observations.*—A feathery crystalline precipitate of the same character and amount is produced in each jar.

#### EXPERIMENT XVII.

*Principle Illustrated.*—The solubility of a salt in water is increased by the addition of a second salt with different ions when there can be produced by metathesis an undissociated substance; and the increase is greater, the greater the amount of this substance formed. Thus, if to saturated solutions of a salt of a partially dissociated acid are added other acids of varying degrees of dissociation, the increase of solubility caused by these will be greater, the greater the degree of their dissociation; for the amount of undissociated acid produced by the metathesis will increase with the increase in the concentration of the hydrogen ions. The formation of the undissociated substance increases the solubility by decreasing the concentration of one of the two ions of the salt saturating the solution, thus making it necessary for more of the salt to dissolve in order to reproduce the original value of the solubility-product.

*Preparation.*—Treat 10 grams of salicylic acid with a solution of 3 grams of anhydrous sodium carbonate in 100 cc. of water; filter; boil to expel carbon dioxide; add a solution of 9 grams of silver nitrate in 100 cc. of water; and wash and dry the precipitate. Place about 1 gram of it and 45 cc. of water in each of four 50 cc. wide-mouthed, glass-stoppered bottles. Place in each of four lecture jars 10 cc. of hydrochloric acid of 1.12 sp. gr. and 250 cc. of distilled water. Place on the lecture table also the half-normal solutions of sulphuric, chloroacetic, and acetic acids used in Expt. VII; a 5 cc. graduated pipette; a stirring rod; four 25 or 50 cc. graduates with a funnel containing a ribbed filter resting in the top of each.

*Experiment.*—Add, with the help of the graduated pipette, 5 cc. of the three half-normal acids to three of the bottles containing the silver salicylate. Shake all four bottles vigorously for half a minute and pour their contents on to the four ribbed filters. Allow 25 cc. to collect in each graduate and pour the four

25 cc. portions into the four jars of dilute hydrochloric acid in the order, water, acetic acid, chloracetic acid, and sulphuric acid.

*Observations.*—The jars to which the water solution and the acetic acid solution are added show a very slight and nearly equal turbidity. The turbidity is much greater in the case of the chloracetic acid, and again much greater in the case of the sulphuric acid.

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## ON THE PREPARATION OF TRIPHENYLCHLORMETHANE.

BY M. GOMBERG.

Received October 4, 1900.

It is generally stated in smaller as well as in larger<sup>1</sup> text-books on organic chemistry, that when carbon tetrachloride is treated with benzene and aluminum chloride triphenylchloromethane is the principal product of the reaction. This statement is entirely erroneous.

Friedel and Crafts, who were the first to study this reaction, reported<sup>2</sup> that they obtained in this way tetraphenylmethane. E. and O. Fischer<sup>3</sup> were unable to verify this result, but could obtain only triphenylmethane. It is to be presumed that they carried on this reaction in a manner analogous to that followed in the preparation of triphenylmethane from chloroform, *i. e.*, the resulting products, after being freed from the chloride of aluminum and the excess of benzene, were subjected to fractional distillation at the high temperature of 200°–360° C. Later, Friedel and Crafts<sup>4</sup> found that the results vary according to the manner of procedure. On distilling the crude products at a high temperature they also obtained triphenylmethane and thus confirmed E. and O. Fischer's results. But if the entire mixture as obtained by the action of aluminum chloride and benzene upon carbon tetrachloride is at once treated with water, it furnishes large quantities of triphenylcarbinol. From this they concluded that the reaction results principally in the formation of triphenylchloromethane,  $(C_6H_5)_3C.Cl$ , and this on treatment with water furnishes the corresponding carbinol. They confirmed this

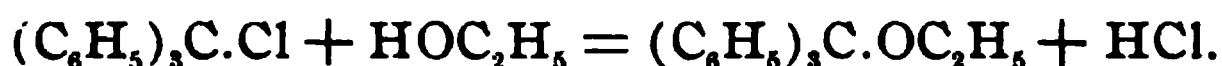
<sup>1</sup> Beilstein: Handbuch, II, 287 (3rd edition).

<sup>2</sup> *Compt. rend.*, 1453 (1877).

<sup>3</sup> *Ann. Chem.* (Liebig), 194, 254.

<sup>4</sup> *Ann. chim. phys.*, I, 497 (1884).

conclusion by the conversion of the crude chloride into the ethoxy compound:



Triphenylmethane is therefore not the first product of the action of benzene upon carbon tetrachloride, but is one of the decomposition products of triphenylchlormethane, formed when the latter is subjected to high heat. That this is likely to occur had been previously shown by E. and O. Fischer on the pure chloro-compound.<sup>1</sup>

Of others who have employed Friedel and Crafts' reaction upon carbon tetrachloride itself or upon its phenylated derivatives may be mentioned Doebner and Magati,<sup>2</sup> Schwartz,<sup>3</sup> Weisse,<sup>4</sup> and V. Meyer.<sup>5</sup> They all report the formation of triphenylmethane,—due, no doubt, in every instance to the subsequent decomposition of the triphenylchlormethane. In this connection, Nencki and Meissel's work may be mentioned. Nencki<sup>6</sup> has shown that ferric chloride may with advantage be substituted for aluminum chloride in many syntheses where Friedel and Crafts' reaction is used. According to Meissel,<sup>7</sup> by the use of this reagent upon a mixture of benzene and carbon tetrachloride, triphenylchlormethane is formed, as by subsequent treatment 75 per cent. of the theoretical amount of triphenylcarbinol can be obtained. "No triphenylmethane is formed in this reaction as is the case when aluminum chloride is employed."

As a matter of fact, however, the action of aluminum chloride upon a mixture of carbon tetrachloride and benzene is exceedingly smooth, provided certain conditions are observed. I have used this reaction many times, and not in a single instance could I detect any trace of triphenylmethane. Friedel and Crafts are entirely correct that triphenylchlormethane is the principal product of the reaction. By observing certain precautions as to temperature of heating and manner of decomposing the chloride of aluminum, the triphenylchlormethane itself can be easily isolated and obtained very pure, with a yield from 70–90 per cent. of the

<sup>1</sup> *Ann. Chem.* (Liebig), 194, 257.

<sup>2</sup> *Ibid.*, 12, 1468.

<sup>3</sup> *Ibid.*, 14, 1523.

<sup>4</sup> *Ibid.*, 28, 1537; 29, 1402.

<sup>5</sup> *Ibid.*, 28, 2792.

<sup>6</sup> *Ibid.*, 30, 1776; 32, 2415.

<sup>7</sup> *Ibid.*, 32, 2422.

theoretical quantity. This forms by far the best method for the preparation of this compound, as by means of it one can easily obtain 500 grams of the pure triphenylchlormethane in less than two days. The chloro compound may, therefore, with advantage replace the triphenylbrommethane in many reactions, as the latter is usually made from the rather expensive triphenylmethane. Even by the method of Allen and Kölliker<sup>1</sup> it cannot always be obtained free from the bromanthracenes.

#### EXPERIMENTAL PART.

*Aluminum Chloride.*—Gattermann<sup>2</sup> called attention to the fact that the yield and smoothness of Friedel and Crafts' reaction depend in a great measure upon the purity of the aluminum chloride. He prepared the latter by the action of hydrochloric acid gas upon heated aluminum. This is at present the method generally employed. Biltz<sup>3</sup> has noticed that in some instances pure, freshly prepared aluminum chloride is rather a detriment, and old, slightly deteriorated reagent is to be preferred. That chlorine acts upon metallic aluminum is a fact well known, but has seldom been employed in laboratories for the preparation of the chloride.<sup>4</sup> I find this to be by far the most convenient method of preparing aluminum chloride, especially when one has access to liquid chlorine. The reagent obtained in this manner is very reactive. About 50 grams of aluminum turnings, thoroughly washed and dried, are placed in a combustion tube, the metal being held in place by loose plugs of asbestos wool. The tube is placed in a combustion furnace, one end is connected with the chlorine tank, and the other fits by means of an asbestos stopper into an iron receiver.<sup>5</sup> The portion of the tube nearest to the receiver is now heated, and a *rapid stream* of dry chlorine is passed into the tube. The gas attacks at once the cold portion of the metal, provided the stream of chlorine is quite rapid. The heat of the reaction is very great, and the metal is kept glowing throughout the length of about 3 inches. In about one and one-fourth to one and one-half hours the reac-

<sup>1</sup> *Ann. Chem.* (Liebig), **227**, 110.

<sup>2</sup> Stockhausen u. Gattermann: *Ber. d. chem. Ges.*, **25**, 3521.

<sup>3</sup> *Ibid.*, **26**, 1960.

<sup>4</sup> My attention is called to the fact that Erdmann recommends this reaction in his "Introduction to Organic Preparations," p. 43.

<sup>5</sup> Gattermann: "Praxis des organischen Chemikers," III. Auflage.



tion is finished. The yield is usually 190–200 grams of aluminum chloride, which represents about 80 per cent. of the theory. Sometimes even 90 per cent. can be obtained. By this method 700–800 grams of the chloride can be prepared in one day by using only one furnace. The reagent prepared in this way is very reactive, and retains this property apparently unimpaired even after being kept for two months.

*Triphenylchlormethane*,  $(C_6H_5)_3C.Cl$ .—The proportions which were found to give good results are 1 part of carbon tetrachloride, 3.5 parts of benzene, and about 1.25 parts of aluminum chloride. The carbon tetrachloride and benzene were thoroughly dried over calcium chloride and carefully fractionated. The two liquids are placed in a round-bottomed flask connected with a long inverted condenser by an arrangement as suggested by Anschütz.<sup>1</sup> The aluminum chloride is added in portions of about 20 grams each. The reaction becomes very violent. I have not attempted to moderate it by cooling. After all the chloride is added, the mixture is heated on the water-bath for about an hour. The next step, the decomposition of the aluminum chloride, requires certain precautions. The cooled mixture is poured in a slow stream upon a good quantity of pounded ice, the jar containing the latter being itself surrounded with a cooling mixture. The addition of the reaction product to the ice should be done slowly, and with constant stirring. Benzene is also added from time to time in order to keep the triphenylchlormethane in solution. After all has been added the benzene solution is separated from the ice and water by a separating funnel, shaken once with ice-water containing hydrochloric acid, and once with ice-water alone. It is advisable to leave the two solutions in contact with each other as short a time as possible. The filtered benzene solution is dried thoroughly over calcium chloride, and concentrated on the water-bath as far as possible. On cooling, over half of the pure triphenylchlormethane separates in large crystals. These are removed by filtration and washed once or twice with dry ether, in which the chloro compound is not very soluble. The filtrate is distilled first on a water-bath at ordinary pressure, and then concentrated by distilling off the benzene under diminished pressure. To the very concentrated solution dry ether is again

<sup>1</sup> *Ann. Chem.* (Liebig), 238, 154.

added, and another large portion of the chloro compound is precipitated. This is treated in the same way as the first crop of crystals, and is just as pure, retaining a slight pink color. The mother liquid is subjected once more to the same treatment—evaporating the ether, and concentrating under diminished pressure—and yields a third crop of crystals. By this treatment the triphenylchlormethane is freed from both the coloring-matter and the triphenylcarbinol, since both of these are quite soluble in ether. The last mother-liquid contains all the coloring-matter. In several instances I have evaporated it to a thick sirup, dried on a porous plate, boiled with water, and obtained considerable quantities of triphenylcarbinol,—but never any indication of triphenylmethane. The yield of the pure chloro compound varies from 70–85 per cent. and enough carbinol can be obtained to account for a yield of 90–95 per cent. of the theory.

In the following table are given some of the results obtained:

	Carbon tetra- chloride. Grams.	Benzene. Grams.	Aluminum chloride. Grams.	Triphenyl- chlor- methane. Grams.	Per cent of theory.	Triphenyl- carbinol Grams.
I .....	300	1000	300	390	72	22
II .....	360	1500	410	500	71	..
III .....	39	150	50	51	78	10
IV .....	129	500	150	201	87	..

It has already been mentioned that the triphenylchlormethane obtained by this reaction is quite pure, and can be employed for most reactions without further purification. It melts usually at  $108^{\circ}$ – $112^{\circ}$  C., while Hemilian<sup>1</sup> gives it as  $105^{\circ}$ – $115^{\circ}$  C.

The following method was found to give equally good results as Carius' for the estimation of chlorine in this substance. The chloro compound is dissolved in alcoholic potash (2 per cent.) and heated for a short time on the water-bath. The alcohol is evaporated, the residue dissolved in water, filtered from the ethyl ether of triphenylcarbinol, and the chlorine is estimated in the filtrate in the usual manner with silver nitrate.

In the following table are given the results of analysis of I, III, IV of the preceding table. The chloro compound had been obtained in three separate crops. Each crop was analyzed by itself.

<sup>1</sup> *Ber. d. chem. Ges.*, 7, 1203.

	First crop.	Second crop.	Third crop.	Calculated for (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> C.Cl.
I.....	12.35	12.74	12.69	12.75
III.....	12.45	12.48	12.49	12.75
IV.....	12.62	12.60	12.56	12.75

The product obtained by this method may, therefore, be considered quite pure. For further purification it can be recrystallized from benzene alone, or better by precipitating it from a concentrated solution in benzene by means of dry ether. By this method large quantities of pure triphenylchlormethane can be more easily obtained than by the old method<sup>1</sup>,—by treating triphenylcarbinol with phosphorus pentachloride.

In conclusion I wish to express my thanks to Messrs. A. G. Marion, H. W. Emerson, and F. L. Woods for their kind assistance in carrying out some of the experimental work.

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## AN INSTANCE OF TRIVALENT CARBON: TRIPHENYLMETHYL.

BY M. GOMBERG.

Received October 4, 1900.

### [PRELIMINARY PAPER.]

SOME time ago<sup>2</sup> I published a method of preparing tetraphenylmethane. The yield was rather small and I was obliged to study the solubilities, composition, molecular weight, and the nitro derivative on about 0.5 gram of the hydrocarbon. The stereochemical interest attached to this compound has induced me to take up the subject once more, in the hope of obtaining larger yields. I have, therefore, gone over most of the methods which have been tried by others for the preparation of tetraphenylmethane. My results, while differing in detail from those published by others, agree in the main,—the hydrocarbon could not be obtained by the usual reactions. One of the main proofs advanced by me for the constitution of tetraphenylmethane was that it furnished a tetranitro derivative which gave no colored salts with alcoholic potash, while most of the less phenylated methanes do respond to this test. To prove whether

<sup>1</sup> Hemilian: *Ber. d. chem. Ges.*, 7, 1207.

<sup>2</sup> *Ber. d. chem. Ges.*, 30, 2043; *This Journal*, 20, 773.

this reaction could safely be relied upon I decided to prepare hexaphenylethane,  $(C_6H_5)_2C-C(C_6H_5)_2$ . This hydrocarbon should by nitration give a hexanitro body with no hydrogen attached to the ethane carbon atoms. Consequently it also should give no colored salts with sodium ethylate or alcoholic potash.

Accordingly, triphenylbrommethane in benzene was treated with metallic sodium, but without success. The chloro compound gave no better results. Molecular silver was substituted for sodium. After several hours' boiling a white crystalline body began to separate, and on filtering the hot benzene solution a considerable amount of the same substance separated on cooling. It was recrystallized from benzene, gave a constant melting-point,  $185^\circ C.$ , and contained no halogen. In its high melting-point and in its only slight solubility in the usual organic solvents it resembled closely tetraphenylmethane, and this new body was taken for hexaphenylethane. An elementary analysis gave, however, the following results :

	Calculated for $(C_6H_5)_6C_2$ .	Found.
Carbon .....	93.83	87.93
Hydrogen .....	6.17	6.04

The low per cent. of carbon found was rather surprising. It was explained on the assumption that this was, perhaps, an instance of a hydrocarbon which is not easily burnt. The next combustion was, therefore, carried on in an atmosphere of oxygen from the very beginning. The substance was mixed in the tube with copper oxide; a very high heat was applied towards the end of the combustion. The results were as follows :

Carbon .....	87.74
Hydrogen .....	6.46

An entirely new lot of the material was then prepared. Ten grams of triphenylchlormethane and 10 grams of silver gave, after several hours' boiling, 4 grams of the same hydrocarbon. This was recrystallized twice from benzene and twice from chloroform. It was perfectly free from halogen, was snow-white, and melted at  $185^\circ-186^\circ C.$  The combustion was again made in an atmosphere of oxygen, lead chromate being used instead of copper oxide.

Carbon .....	87.77
Hydrogen .....	6.23

The next analysis was made in a bayonet tube, the tube being filled with fine copper oxide for about four-fifths of its length, to insure combustion of any methane gas which would perhaps otherwise escape. The combustion was carried on slowly, and a very high heat was used towards the end.

Carbon .....	88.23
Hydrogen .....	6.34

Several new lots of the same substance were made both from the triphenylbrommethane and triphenylchlormethane, and purified by successive recrystallization from benzene, chloroform, acetic ether, and carbon disulphide. They all gave the same results, entirely concordant with each other. Combustions were then made in a porcelain tube, applying the direct heat of the furnace; also by the moist method with chromic acid in concentrated sulphuric acid,<sup>1</sup> but with no better result. I therefore came to the conclusion that the body under consideration was not a simple hydrocarbon, but an oxygen derivative. The oxygen could come from either of two sources: first, the molecular silver may have contained some oxide of the metal; second, the atmospheric oxygen may act upon the hydrocarbon.

As only the molecular silver, and not the finely powdered crystalline metal appeared to act in this case, a very pure sample of the former was prepared. The moist silver, as obtained by reduction of the chloride with zinc, was digested for a day with dilute sulphuric acid. It was then thoroughly washed by decantation, digested for several hours with ammonium hydroxide, again washed with water, then with alcohol, absolute alcohol, ether, and finally with benzene. This sample of silver gave, however, results not differing from those previously obtained. To make it more certain that the oxygen did not come from the silver, I substituted other metals for it. Mercury and zinc were found to act equally well, if not better, and the yield of the oxygen compound obtained by either of these two metals was even greater than in the case of silver. Another great advantage in the use of zinc and mercury is that the reaction takes place at *ordinary temperature*. Mercury is especially well suited for a

<sup>1</sup> Fritzsche: *Ann. Chem.* (Liebig), 294, 79.

lecture experiment showing this reaction. If a benzene solution of triphenylchlormethane or triphenylbrommethane be shaken in a test-tube for a few minutes with some metallic mercury and the solution rapidly filtered, the separation of the insoluble oxygen compound in the filtrate will soon begin, due to the absorption of atmospheric oxygen.

I next proved that it is really the oxygen from the atmosphere which oxidizes the hydrocarbon. By working in an atmosphere of carbon dioxide no such insoluble compound is produced, even on weeks' and months' treatment of the halogen bodies with silver, mercury, or zinc in benzene. After a long series of experiments I settled upon zinc as the best reagent with which to carry on this reaction. Ordinary granulated zinc, zinc strips, zinc dust,—all act upon the halogen compounds. In all further experiments what is known as *powdered zinc*, freed from zinc dust by sifting, has been employed. In this form the metal can readily be obtained free from the oxide, is easily handled, has a large surface exposure, and presents no difficulties in filtering from the benzene solution. Triphenylchlormethane<sup>1</sup> has been used altogether instead of the bromine compound.

The successful preparation of the unsaturated hydrocarbon requires the *absolute* exclusion of oxygen from the apparatus. Corks are to be avoided, and even rubber stoppers, exposed to the action of benzene vapors, become after a while porous. I have constructed for this work an apparatus by means of which the reaction can be carried on for several weeks, and months, if necessary. The zinc, benzene, and triphenylchlormethane are first digested for any length of time desired at ordinary temperature; the solution is then filtered into a distilling flask and the zinc washed with fresh portions of benzene. The combined liquids are distilled under diminished pressure at 30° C., and the solid crystalline residue containing the unsaturated hydrocarbon can be examined as to its solubility in different solvents, or treated in any manner desired. The apparatus is so arranged that all these steps are carried on in an atmosphere of dry carbon dioxide. Only ground-glass joints are used. The description of the apparatus is reserved for a future paper.

<sup>1</sup> For the preparation of this see the preceding paper.

## I. THE HALOGEN IS TAKEN OUT BY THE ZINC QUANTITATIVELY.

The zinc removes the halogen from triphenylchlormethane quantitatively at ordinary temperature. The zinc chloride separates as a thick dark yellow sirup, probably forming a compound with benzene similar to the one produced by aluminum chloride. This is of very great advantage, because by this means fresh, clean surfaces of the metal are continually exposed for further action. For this reason the reaction is very slow, and soon stops altogether when carbon tetrachloride is substituted for benzene. With 20 grams of triphenylchlormethane, 150 grams of benzene, and 25 grams of zinc the reaction is completed in about five to six days. After removing the benzene solution and washing the residue thoroughly with benzene, the zinc chloride was dissolved in water and the chlorine estimated in the usual way.

	Triphenyl- chlormethane taken. Grams.	Number of days of digestion.	Chlorine as ZnCl <sub>2</sub> .	Calculated.
I .....	5	12	12.61	12.75
II .....	20	5	12.25	12.75
III .....	20	20	12.41	12.75

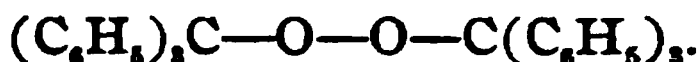
## II. THE UNSATURATED HYDROCARBON.

The clear filtered solution containing the unsaturated hydrocarbon is concentrated under diminished pressure at a temperature of 30°–35° C., a slow stream of carbon dioxide being used to prevent bumping. When all the benzene has been distilled off, a strong stream of the gas is allowed to bubble through the thick yellow sirup, while the temperature is raised to about 40° C. On cooling, the whole residue solidifies to a crystalline cake, which does not melt even at 60° C. Even after several weeks' standing it redissolves readily in benzene with the exception of some of the oxygen compound whose formation is due to unavoidable leakage of the stop-cocks. The hydrocarbon is quite soluble in chloroform, less so in carbon tetrachloride, and is quite readily dissolved by carbon disulphide. If a concentrated solution of it is allowed to stand for three or four weeks, some large transparent crystals are formed. An attempt was made to remove these and wash with petroleum ether, but before the operation was finished enough oxygen was absorbed to form the

insoluble derivative. I hope to be able to isolate the hydrocarbon itself in a pure state.

The body is extremely unsaturated. A solution of it in benzene or in carbon disulphide absorbs oxygen with great avidity and gives an insoluble oxygen compound. It absorbs chlorine, bromine, and iodine. It does not unite with carbon monoxide.<sup>1</sup>

### III. DI-TRIPHENYLMETHYLPEROXIDE,



The crystalline compound which is formed by the action of the atmospheric oxygen upon a solution of the unsaturated hydrocarbon, is the peroxide of triphenylmethyl. It is best prepared by passing air or oxygen through a solution of the hydrocarbon in benzene. Twenty grams of the halogen compound give about 12 grams of the peroxide. The elementary composition fully agrees with that required by the formula :

	Calculated for (C <sub>6</sub> H <sub>5</sub> ) <sub>6</sub> C <sub>2</sub> O <sub>2</sub> .	I.	II.	Found. III.	IV.	V.
Carbon.....	88.03	87.93	87.74	87.77	88.22	87.60
Hydrogen.....	5.79	6.04	6.46	6.23	6.34	6.09

This body is characterized by extreme insolubility. It is only with difficulty dissolved by hot benzene, toluene, and then not without some decomposition. It can be recrystallized from chloroform. It is insoluble in ether, alcohol, and water. It is best recrystallized from carbon disulphide, 1 gram dissolving in about 150 cc. of the hot solvent. I have obtained by the use of this solvent remarkably beautiful and regular crystals, six-sided hexagons, of a very high refractive index. The peroxide melts at 185°-186° C. (uncorr.)

It is quite stable on exposure to air but decomposes gradually when a solution of it is heated. For this reason solvents of low boiling-point are to be preferred.

*Formation by Means of Sodium Peroxide.*—On heating triphenylchlormethane in benzene with commercial barium peroxide for several days a small amount of the triphenylperoxide was obtained. On repeating the experiment with a purified sample of barium peroxide the result could not be duplicated. I have resorted to the use of sodium peroxide, and with this

<sup>1</sup> Compare Nef: *Ann. Chem.* (Liebig), 270, 267.



reagent I never failed to get the peroxide. A 10 per cent. solution of sodium peroxide is made by dissolving the latter in ice-water. Three to four grams of triphenylchlormethane in just enough benzene to make a clear solution are added, and a stream of air, free from carbon dioxide, is passed through the cold mixture until all the benzene is evaporated. The air keeps the two liquids in constant motion and fresh quantities are continually exposed to action. The solution is now filtered and washed. The unchanged chloro compound and the carbinol are removed by ether and the insoluble residue is boiled up with a large amount of carbon disulphide. The filtered solution gives, on concentration, a small amount of the characteristic crystals of the peroxide. This method was repeated several times, with and without the use of benzene, and has invariably given from 5 to 10 per cent. of the calculated amount of the peroxide. The larger portion of the chloride is changed to the carbinol, as it always does when left in contact with water, especially in presence of alkalies. The peroxide so obtained was identical with the one previously described. An analysis gave the following figures :

	Calculated for (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> C <sub>2</sub> O <sub>2</sub> .	Found.
Carbon .....	88.03	87.55
Hydrogen .....	5.79	6.00

That the formation of the peroxide is really due to the presence of sodium peroxide, and does not result from the oxidation of the chloride or the carbinol by atmospheric oxygen, is shown by the following experiment: Three grams of the chloride dissolved in 10 cc. of benzene, were added to 100 cc. of a 10 per cent. solution of sodium hydroxide, and air was passed through the flask exactly in the same way as when sodium peroxide was used. On working up the product not a trace of triphenylmethylperoxide was found.

*Molecular Weight.*—Attempts to get an exact determination of the molecular weight have not proved as successful as desired. The peroxide is only slightly soluble in the usual organic solvents, and, therefore, only a slight elevation of the boiling-point could be expected, from 0.003°-0.150° C. I have found no liquid or low-melting solvent which could be used for the freezing-point

method. In using the boiling-point method it was found necessary to select as low-boiling a solvent as possible, since the peroxide suffers gradual decomposition at higher temperatures. Carbon disulphide was tried first. As the solubility of the peroxide in this solvent is only about 1 gram in 150 cc., the maximum rise of temperature could not be expected to be above  $0.040^{\circ}$  C. I therefore constructed an apparatus similar to the one described by Jones.<sup>1</sup> From 100–200 grams of the solvent could then be employed for a single determination. By this means the influence of the absolute error due to the weighings, vaporization of the solvent, etc., is greatly reduced. The apparatus proved very reliable, and the solvents employed could be kept boiling for an hour with a variation of temperature not exceeding  $0.002^{\circ}$  C. Tested on triphenylmethane the apparatus gave a molecular weight of 252 (244 calculated) when 1.2862 grams of the substance and 113 grams of the solvent were employed. The rise of temperature was to  $0.107^{\circ}$  C.

SOLVENT : CARBON DISULPHIDE.  $K = 2370$ .

Carbon disulphide. Grams.	Peroxide. Gram.	Rise in boiling-point.	Calculated rise for $m = 518$ .	Molecular weight.
121.7	0.7300	0.035	0.028	406

The temperature remained constant for about fifteen to twenty minutes; after that it gradually began to rise, about  $0.001$  every ten minutes. The experiment was interrupted when  $0.045$  was reached. The solution was yellowish, showing slight decomposition of the peroxide.

SOLVENT : BENZENE.  $K = 2770$ .

Benzene. Grams.	Peroxide. Grams.	Rise in boiling-point.	Calculated rise for $m = 518$ .	Molecular weight.
66	0.853	0.09	0.070	448

This temperature remained constant for about ten minutes, after that the rise was gradual until in an hour it reached  $0.185^{\circ}$  C. The solution was then quite yellow.

Ethylene dibromide was also tried, but as this boils still higher, there was even more rapid decomposition. The results in the main agree with those obtained when benzene was used.

The only conclusion that can be safely drawn from these results is that we have here a substance of very high molecular

<sup>1</sup> *Am. Chem. J.*, 19, 581.

weight, above 400 at least. The formula for the peroxide would require 518.

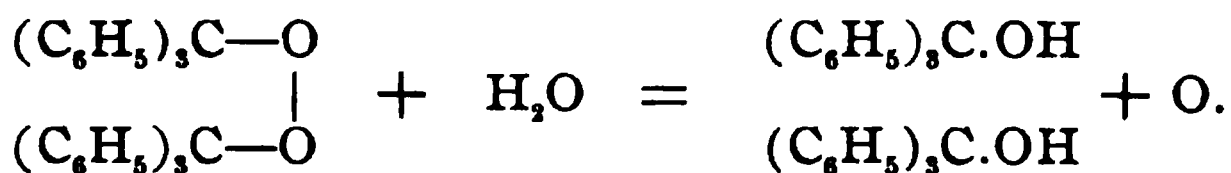
*Conversion of the Peroxide into the Carbinol.*—The peroxide dissolves in cold concentrated sulphuric acid with considerable evolution of heat, giving a yellow solution which soon turns dark, and finally almost black. The sulphuric acid does not induce any explosion as is the case with most organic peroxides. On diluting the acid with water the triphenylcarbinol is precipitated out as a dark flocculent precipitate.

2.85 grams of the pure peroxide were dissolved in 25 cc. of sulphuric acid and allowed to stand over night. The solution was then poured upon ice and the precipitate separated by filtration. It was dissolved in ether, and the dark ethereal solution was repeatedly shaken with dilute sodium hydroxide until the ether was only of a pale yellow color. The dried ethereal solution was then concentrated to a small bulk and rhigolene added. Crystals of triphenylcarbinol separated and were almost pure, melting at 159°–160° C. The yield was 1.948 grams, which represents 70 per cent. of the peroxide taken. The mother-liquid, on concentration, gave additional 0.215 gram, and 0.050 gram was obtained from the third crop, making a total of almost 80 per cent. The remaining 20 per cent. were probably oxidized by the oxygen evolved or perhaps sulphonated, as the sodium hydroxide removes all the dark color from the ethereal solution. An analysis gave the following results :

0.2910 gram substance gave 0.9330 gram carbon dioxide and 0.1654 gram water.

	Calculated for (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> C.OH.	Found.
Carbon .....	87.69	87.44
Hydrogen .....	6.15	6.31

The reaction may therefore be represented by the following equation :



*Di-trinitrotriphenylmethylperoxide*, (C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)<sub>3</sub>C—O—O—C(C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)<sub>3</sub>.—Brodie,<sup>1</sup> Vanino,<sup>2</sup> and Nef<sup>3</sup> have shown that the

<sup>1</sup> *Ann. Chem.* (Liebig), Suppl. III, 209.

<sup>2</sup> *Ber. d. chem. Ges.*, 30, 2004; 33, 1045.

<sup>3</sup> *Ann. Chem.* (Liebig), 298, 287.

superoxides of acid radicals can be nitrated with fuming nitric acid. The peroxide here described shares the same property. It forms very readily a hexanitro compound. One gram of the peroxide gave 1.375 grams of the pure nitro body, while theory requires 1.555 grams. The nitro compound is insoluble in the usual organic solvents. One gram refuses to dissolve completely in 500 cc. of boiling glacial acetic acid. It is best recrystallized by dissolving it in nitrobenzene at 120°–130° C., and precipitating with petroleum ether.

	Calculated for $C_{20}H_{24}N_6O_{14}$	I.	Found.	II.
Carbon.....	57.87	57.55		....
Hydrogen.....	3.05	3.34		....
Nitrogen.....	10.65	11.03		10.94

#### IV. TRIPHENYLIODOMETHANE, $(C_6H_5)_3C.I.$

The unsaturated hydrocarbon, which is formed when the halogen is removed from triphenylchlormethane, unites not only with oxygen, but also instantly with chlorine, bromine, and iodine. The reaction with chlorine and bromine is, however, not one of mere addition. The hydrocarbon is so reactive that even at –10° C. chlorine and bromine act both by addition and substitution. When the hydrocarbon, entirely freed from benzene, is dissolved in carbon tetrachloride there is always some hydrochloric and hydrobromic acid produced on the addition of the halogen. Triphenylchlormethane and triphenylbrommethane are among the products but it is not easy to separate the substitution halogen-compounds formed at the same time. This reaction will be further studied.

*Iodine is absorbed* by the hydrocarbon as readily as the other two halogens. When a solution of the hydrocarbon in carbon disulphide is treated at 0° C. with a solution of iodine in the same solvent, the latter is instantly decolorized. The end-reaction is quite sharp. In one instance, working with a product from 20 grams of triphenylchlormethane, 6 grams of iodine were absorbed, which is equivalent to 12 grams of  $(C_6H_5)_3C-$ ; in another case, where 25 grams of the chloro compound were employed, the absorption amounted to 8 grams of iodine. The isolation of the iodo compound requires considerable precautions, as it is a very

unstable body. I have found it best to work in an atmosphere of dry carbon dioxide, but am not as yet prepared to say whether it is the oxygen or the moisture of the air that affects it most. Probably it is the latter. The solution of the iodo compound was filtered to remove a slight amount of a periodide<sup>1</sup> and the peroxide. To the clear carbon disulphide solution rhigolene was added and the mixture cooled in ice. After some crystals had separated the liquid was transferred to another flask and cooled again, when more crystallized out. This last crop was recrystallized by dissolving it in carbon disulphide and precipitating with rhigolene. The crystals were of a pale yellow color, the same in appearance as the chloro compound when the latter is similarly precipitated. The crystals were washed several times with rhigolene and dried rapidly *in vacuo*.

The iodine was estimated by treating a weighed sample of the compound in dilute alcohol with ammonia and zinc dust. The hot alcoholic solution was filtered, the zinc washed thoroughly with hot alcohol, and then with water. The alcohol washings were concentrated, filtered, and the residue was exhausted with water. The insoluble portion was purified with ether, and was identified as triphenylcarbinol. It melted at 153° C., probably due to the presence of some triphenylmethane. On recrystallizing twice from alcohol the melting-point was raised to 157°–159° C. The yield of the carbinol was 0.383 gram, while the calculated quantity for the 0.602 gram of triphenyliodomethane was 0.422 gram.

0.602 gram substance gave 0.3704 gram AgI.

	Calculated for (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> C.I.	Found.
Iodine.....	34.29	33.23

The iodide turns dark very readily and loses iodine. It is very unstable. It melts approximately at 135° C., with decomposition. Water, especially in the presence of alkalies, converts it into triphenylcarbinol, a reaction similar to that with the corresponding chloro and bromo compounds. Alcohol, however, behaves in this case differently. On boiling with alcohol large quantities of iodine are set free and the body is reduced by the

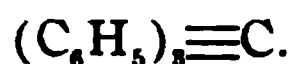
<sup>1</sup> For a periodide of triphenylbrommethane, see this Journal, 20, 790.

alcohol to triphenylmethane, while in the case of triphenylchloromethane and triphenylbrommethane the ethyl ether,

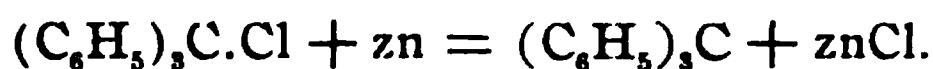


is formed. The triphenylmethane was freed from a small amount of the unreduced ether by fractional crystallization from alcohol, and was identified by its characteristic crystals containing benzene of crystallization and melting at  $77^\circ\text{C}$ . On exposure to air the benzene of crystallization was lost and the crystals melted at  $92^\circ\text{C}$ .

#### V. TRIPHENYLMETHYL,



The experimental evidence presented above forces me to the conclusion that we have to deal here with a free radical, triphenylmethyl,  $(\text{C}_6\text{H}_5)_3\equiv\text{C}$ . On this assumption alone do the results described above become intelligible and receive an adequate explanation. The action of zinc results, as it seems to me, in the mere abstraction of the halogen, leaving the free radical,

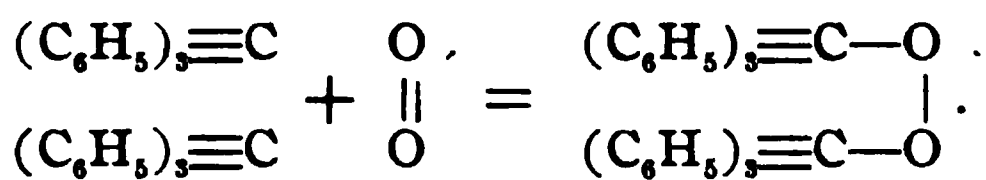


The radical so formed is apparently stable, for it can be kept both in solution and in the dry crystalline state for weeks. The radical refuses to unite with another one of its kind, and thus forms a distinct exception to all similar reactions. It might be said that, perhaps, it does polymerize to hexaphenylethane,  $(\text{C}_6\text{H}_5)_3\text{C}-\text{C}(\text{C}_6\text{H}_5)_3$ , but this hydrocarbon is so unstable that mere exposure to air is sufficient to break it down. Such an assumption seems to me less tenable than that of a free radical. Hexaphenylethane must, according to all our present notions of valence, be a saturated compound. Yet the hydrocarbon under consideration is decidedly unsaturated. We know of no better positive test for unsaturation in hydrocarbons than the absorption of halogens. Perhaps chlorine and bromine would in this case attack and decompose hexaphenylethane, if that be the hydrocarbon; but, certainly, a dilute solution of iodine, at  $0^\circ\text{C}$ ., would scarcely do that. It seems to me rather that hexaphenylethane, once formed, would prove quite a stable compound. This may be justly inferred from analogous reactions, where a

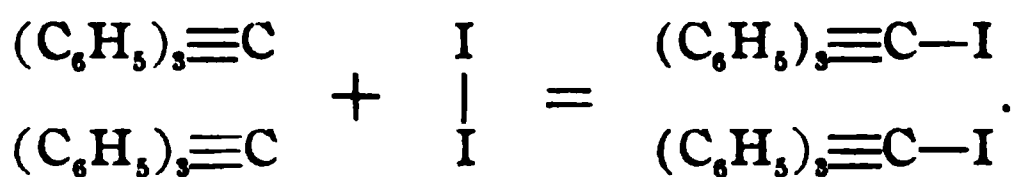
<sup>1</sup> Hemilian: *Ber. d. chem. Ges.*, 7, 1208.

fourth heavy radical has been successfully introduced into the methane,—as is the case with triphenylthiophylmethane,  $(\text{C}_6\text{H}_5)_3\text{C}.\text{C}_4\text{H}_4\text{S}$ ,<sup>1</sup> tetraphenylmethane,  $(\text{C}_6\text{H}_5)_4\text{C}$ ,<sup>2</sup> triphenylacetic acid,<sup>3</sup> etc. It is a phenomenon parallel to that expressed by V. Meyer's esterification law of diortho substituted aromatic acids : It is very difficult to introduce an alkyl into the carboxyl of such acids by the *usual method* of esterification, but once introduced, it is just as difficult to remove it again.

On the assumption of the existence of triphenylmethyl itself, as such, all the reactions of the unsaturated body become clear. Oxygen adds itself, a whole molecule, and gives the peroxide :



The addition of a molecule of oxygen is entirely in accord with the recent studies of M. Traube, van 't Hoff, Engler, Manchot, Bach, Baeyer and Villiger, and Nef. This case forms an excellent illustration of Engler's<sup>4</sup> theory that "autoxidation" results first of all in the formation of superoxides. The action of halogens upon the unsaturated body is primarily that of addition. Thus iodine gives triphenyliodomethane :



That the unsaturated hydrocarbon is not the result of some complicated reaction between triphenylchlormethane, benzene, and the nascent zinc chloride formed during the experiment, is proved by the following : 5 grams of the halogen compound were dissolved in 100 cc. of carbon disulphide and shaken at intervals with 100 grams of metallic mercury for two days. The clear filtered solution on exposure to air furnished 3.8 grams of triphenylmethyl peroxide. Five grams of triphenylchlormethane, treated with zinc and benzene for four days, gave 3.1 grams of the peroxide.

The existence of triphenylmethyl implies, of course, the existence of *trivalent carbon*, at least in this particular instance. The

<sup>1</sup> Weisse : *Ber. d. chem. Ges.*, 28, 1538.

<sup>2</sup> Gomberg : *Ibid.*, 30, 2043.

<sup>3</sup> E. and O. Fischer : *Ann. Chem. (Liebig)*, 194, 260; Heyl and V. Meyer : *Ber. d. chem. Ges.*, 28, 2782.

<sup>4</sup> *Ber. d. chem. Ges.*, 30, 1669; 33, 1090, 1097.

conception of such a trivalent carbon in this instance is entirely distinct from that which is ascribed to it by some in benzene, or even in ethylene, where there are always *two* adjoining carbon atoms acting as trivalent. The unsaturation in such cases has always been indicated by a "double linking." In triphenylmethyl there is *only one carbon atom* that is unsaturated. The existence of such a body means that when three valences of carbon are taken up by three phenyl groups it is difficult, or perhaps even impossible, to introduce as a fourth group such a complicated radical as  $(C_6H_5)_3C-$ . Only simpler groups, chlorine, bromine, iodine, oxygen, etc., may still combine with such a carbon atom. Whether this be due to the negative character of the three phenyl groups, or whether it is caused by the fact that these groups take up so much space around the carbon atom as to hinder the introduction of another complicated group, is a question of an entirely different nature and need not be discussed here. There are, however, numerous reactions which go to show that there is a limit to the number of complicated groups which can ordinarily be linked to one and the same carbon atom. A few of these reactions may be mentioned.

Hemilian,<sup>1</sup> Friedel and Crafts,<sup>2</sup> E. and O. Fischer,<sup>3</sup> Magati,<sup>4</sup> Schwartz,<sup>5</sup> V. Meyer,<sup>6</sup> Weisse,<sup>7</sup> Waga,<sup>8</sup> and Meisel,<sup>9</sup> have all attempted to prepare tetraphenylmethane, but in all cases triphenylmethane resulted. Even such comparatively simple compounds as  $(C_6H_5)_3C.C_2H_5$ ,<sup>10</sup> or  $(C_6H_5)_3C.CH_3$ ,<sup>11</sup> could not be obtained by reactions from which, *a priori*, we should certainly expect the formation of such bodies. The disinclination of carbon to hold more than three complicated groups is well illustrated by the results of Anschütz's<sup>12</sup> extended researches on tetraphenylethane. A large number of methods which ought to give the unsymmetrical derivative,  $(C_6H_5)_3C.CH_2(C_6H_5)$ , always

<sup>1</sup> *Ber. d. chem. Ges.*, 7, 1209.

<sup>2</sup> *Ann. chim. phys.*, 1884, I, 497.

<sup>3</sup> *Ann. Chem. (Liebig)*, 194, 254.

<sup>4</sup> *Ber. d. chem. Ges.*, 12, 1468.

<sup>5</sup> *Ibid.*, 14, 1523.

<sup>6</sup> *Ibid.*, 28, 2792.

<sup>7</sup> *Ibid.*, 28, 1538; 29, 1402.

<sup>8</sup> *Ann. Chem. (Liebig)*, 282, 330.

<sup>9</sup> *Ber. d. chem. Ges.*, 32, 2422.

<sup>10</sup> E. and O. Fischer: *Ann. Chem. (Liebig)*, 194, 259.

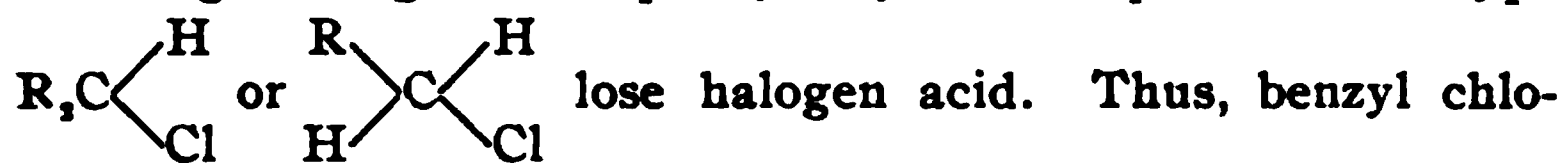
<sup>11</sup> Biltz: *Ibid.*, 296, 253.

<sup>12</sup> *Ibid.*, 235, 203.



give the symmetrical one,  $(C_6H_5)_2CH.CH(C_6H_5)_2$ . And lastly, the abnormal behavior of tetraphenylethylene towards bromine, as found by Biltz,<sup>1</sup> shows again the same point. Bromine will substitute in, but not add itself to, tetraphenylethylene, although we have here an unsaturated linking,  $(C_6H_5)_2C : C(C_6H_5)_2$ . These and a number of other facts show conclusively that with three valences of carbon taken up by such complicated or large groups as phenyl, the fourth valence can ordinarily be linked to atoms or groups of simple construction only. Now, as a result of the removal of halogen from triphenylchlormethane in benzene by zinc, or in carbon disulphide by mercury, the fourth valence of the methane carbon is bound either to take up the complicated group  $(C_6H_5)_2C-$ , and polymerize, or remain as such, with carbon as trivalent. Apparently the latter is what happens.

In conclusion, it may be mentioned that the action of metals upon triphenylhalogenmethane has been tried before. Elbs<sup>2</sup> acted upon triphenylbrommethane with sodium, magnesium, and copper. Anschütz<sup>3</sup> employed sodium upon a mixture of triphenylbrommethane and benzyl chloride. The action of metals upon the di- and monophenylhalogen methanes has also been extensively studied. While diphenyldichlormethane loses all its halogen and gives tetraphenylethylene, compounds of the type



ride, when treated with zinc,<sup>4</sup> zinc-copper couple,<sup>5</sup> gives polymers and reduction-products of phenylmethylene. Recently Nef<sup>6</sup> has used aluminum chloride upon benzyl bromide in the hope of splitting off hydrobromic acid and thus obtaining the free radical phenylmethylene,  $(C_6H_5)CH$ . The formation of the latter as an intermediate product was made quite probable, but the isolation of it proved impossible, owing to a rapid polymerization.

This work will be continued and I wish to reserve the field for myself.

UNIVERSITY OF MICHIGAN,  
CHEMICAL LABORATORY,  
August, 1900.

<sup>1</sup> Ann. Chem. (Liebig), 296, 231.

<sup>2</sup> Ber. d. chem. Ges., 17, 700.

<sup>3</sup> Ann. Chem. (Liebig), 235, 226.

<sup>4</sup> Zinke: *Ibid.*, 159, 1368.

<sup>5</sup> Gladstone and Tribe: *J. Chem. Soc.*, 45, 154; 47, 448.

<sup>6</sup> Ann. Chem. (Liebig), 298, 248.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 52.]

## THE SEPARATION OF TUNGSTEN TRIOXIDE FROM MOLYBDENUM TRIOXIDE.

BY MAX J. RUEGENBERG AND EDGAR F. SMITH.

Received September 7, 1900.

THE separation of tungsten from molybdenum is always of interest to those who are brought in contact with analytical methods. It has been the subject of numerous investigations and much discussion, and while comparatively good methods exist for this purpose, the analyst continues to seek for others, hoping that eventually he shall find a procedure which will be satisfactory in all respects and under nearly all conditions.

The writers have not discovered the method *par excellence*, but desire to offer briefly, in the following lines, their experience in pursuing a suggestion made in an article emanating from this laboratory; *viz.*, "tungstic acid is . . . . insoluble in concentrated or dilute sulphuric acid, hot or cold, whereas molybdenum trioxide is very easily and rapidly dissolved, so that we have in this department a very simple and exact method for the separation of the two metals."<sup>1</sup>

No analytical data accompanied this declaration; therefore it seemed not improper to attempt to learn the conditions most favorable for the separation. Upon trial it was found that sulphuric acid of specific gravity 1.378, dissolved molybdenum trioxide very readily and apparently did not affect the tungsten trioxide. Acid of this concentration was, therefore, used with the following mixture of the two oxides:

I. 0.7355 gram of tungsten trioxide and 0.0185 gram of molybdenum trioxide were digested for a few minutes with 25 cc. of warm sulphuric acid. The insoluble portion was filtered out and washed with water containing sulphuric acid. After drying it was ignited and weighed. It equaled 0.7350 gram.

The other trials, conducted in precisely the same manner, were as follows:

	II. Grams.	III. Grams.	IV. Grams.	V. Grams.	VI. Grams.
Tungsten trioxide taken . . . .	1.0638	0.0871	0.3588	0.8868	0.5996
Molybdenum trioxide taken	2.2712	0.6871	1.1836	1.1986	1.0770
Tungsten trioxide found . . .	1.0630	0.0870	0.3587	0.8866	0.5996

<sup>1</sup> En. D. Desi: This Journal, 19, 242.

The filtrate containing the dissolved molybdic acid showed no tungstic acid upon examination.

These results indicate that where the two oxides are present together this mode of separation is apparently of value and merits consideration.

A weighed quantity of a ferric salt equivalent to 5 grams of ferric hydroxide was precipitated with ammonia water and the resulting precipitate, after being washed, was mixed in a beaker with different amounts of tungsten trioxide, and the resulting mixture was then digested with sulphuric acid of the strength of that used in the preceding experiments. The residual oxide was treated as before :

	I.	II.	III.	IV.	V.	VI.
	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.
Tungsten trioxide taken ..	0.5282	0.2087	1.3270	0.2004	0.9091	0.2263
Ferric hydroxide taken ...	5.0000	5.0000	5.0000	5.0000	5.0000	5.0000
Tungsten trioxide found ..	0.5278	0.2086	1.3265	0.2003	0.9088	0.2262

We may conclude from these trials that the solubility of the trioxide in the sulphuric acid is in no wise affected by the presence of the iron.

UNIVERSITY OF PENNSYLVANIA.

## NEW BOOKS.

**THE MINERAL INDUSTRY: ITS STATISTICS, TECHNOLOGY, AND TRADE IN THE UNITED STATES AND OTHER COUNTRIES, TO THE END OF 1899.** EDITED BY RICHARD P. ROTHWELL. Vol. VIII. Large 8vo. xxviii+986 pp. With many illustrations. New York: The Scientific Publishing Co. Price, \$5.00.

This new annual volume of a well-known and greatly valued series fully sustains the reputation already obtained. The difficulty in obtaining accurate information of this character is well known, and the rapid publication of a large volume like this, requiring the cooperation of so many persons, reflects the greatest credit upon all those concerned in it. The year 1899 was a great year for the mineral industry in the United States, the production in nearly all metals and minerals showing a decided increase. This is especially noticeable in Portland cement, where the increase is from 3,584,586 barrels of 400 lbs. in 1898 to 5,805,620 barrels in 1899. Among the new products listed in recent years are ferromolybdenum, 6,000 lbs. in 1899; molybde-

num, 30,000 lbs.; tungsten, 45,000 lbs.; and Fuller's earth, 13,360 tons.

Among special articles of note are those on "Progress in the Aluminum Industry," by John B. C. Kershaw; "The Occurrence and Genesis of Californian Asphalt," by A. S. Cooper; "Notes on the Metallurgy of Bismuth," by W. Borchers; "Calcium Carbide," by John B. C. Kershaw; "The Hydraulic Cement Industry in the United States in 1899," by Frederick H. Lewis; "Notes on the Metallurgy of Chromium," by W. Borchers; "Notes on the Coarse Pottery Production of Great Britain," by Wilton P. Rix; "Fuel and Its Economical Utilization," by William Kent; "Progress in the Electrolytic Refining of Copper during 1899," by Titus Ulke; "Hofmann's Method for the Manufacture of Blue Vitriol," by Ottokar Hoffmann; "The Cutting and Polishing of Precious Stones," by Leopold Claremont; "Glass," by Robert Linton; "Rare Elements," by Victor Lenher; "The Electrolytic Production of Caustic Soda," by Alfred T. Weightman; "The Manufacture of Sulphuric Acid Stronger Than Chamber Acid," by F. J. Falding; and "The Sulphur Industry of Italy," by Giovanni Aichino.

This list is only a partial one. Many of the articles are illustrated, and not a few contain real contributions to the literature of the subjects treated. E. H.

ANNALI DEL LABORATORIO CHIMICO CENTRALE DELLE GABELLE DIRETTI DEL DR. VITTORIO VILLAVECCHIA. VOL. IV. Roma Tipografia Elzeviriana, di Adelaide ved. Pateras. 1900. 528 pp.

The report of the Central Chemical Laboratory of the Italian Customs, Vol. IV, by Dr. Vittorio Villavecchia for the years 1898 and 1899 contains nineteen papers or reports on the methods of analysis or examinations of the character of manufactured articles and natural products which are of commercial importance to the country. They comprise the following.

1. "The Composition of Wines Imported into Italy during the Period from 1890-1897." V. Villavecchia.

2. "Methods for the Analysis of the Essential Oils of Bitter Fruits (Lemon, Orange, Bergamot)." G. Fabris. Contains interesting details of the methods of extraction as well as an account of the composition of the pure essences and the methods of detecting adulteration. The principal adulterant seems to be

oil of turpentine but the detection of its presence in small proportion does not seem very certain.

3. "Artificial Turpentine." G. Fabris.

4. "On the Analysis of Coal Tar and Its Preparations." G. Fabris.

5. "Contribution to the Analysis of Oils." M. Tortelli and R. Ruggieri.

I. The detection of cottonseed oil, oil of sesame, and peanut oil in olive oil.

II. The quantitative determination of peanut oil.

6. "A Method for Determining the Absolute Iodine Index of Fatty Substances." M. Tortelli and R. Ruggieri.

7. "The Oil and Wax (Vegetable Tallow) of the *Stellingia Sebifera*." M. Tortelli and R. Ruggieri.

8. "The Composition and Analysis of Vermouth." A. Bianchi.

9. "A Modification of Milliau's Test for the Presence of Cottonseed Oil." G. Armani.

10. "Boiled Vegetable Oils and Their Detection in Admixture with Other Oils." Tortelli and Ruggieri.

11. "The Quantitative Determination of Invert Sugar and Glucose in the Presence of Dextrine." A. Bianchi.

12. "The Determination of the Point of Solidification of Fatty Acids." R. Morischini.

13. "The Analysis and Composition of Certain Qualities of Commercial Bread." G. Fabris and D. Marino.

14. "On the Heating of Certain Gums Used in the Manufacture of Varnishes." G. Armani.

15. "The Characteristics and the Illuminating Power of Stearine, Paraffin, and Spermaceti Candles." R. Ruggieri.

16. "A Contribution to the Knowledge of the Distinctive Characteristics and the Illuminating Power of American Petroleum as Compared with the Russian." G. Rossi.

17. "The Chemical Analysis of Commercial Inks." G. Malagnini.

18. "A Study of the So-called Spices or Powdered Condiments of Commerce." S. Camilla.

19. "Artificial Silks and the Tests to Distinguish Them from Natural Silks." A. Salaro.

Most of these papers are interesting and valuable but from their nature they are difficult to abstract.

The number of samples examined in the laboratory in 1898 was 6,158; in 1897, 5,533. The majority of these consisted of beer, wine, and oils, but almost everything dutiable is represented.

ANDREW A. BLAIR.

(1) **EXPERIMENTAL CHEMISTRY.** BY L. C. NEWELL. 12 mo. xvi + 410 pp. 114 illustrations. D. C. Heath & Co. Price, \$1.10.

(2) **THE ELEMENTS OF INORGANIC CHEMISTRY.** BY W. A. SHENSTONE. London: Edward Arnold. 12mo. xii + 506 pp. 142 illustrations.

(1) The purpose of this book, as the preface states, "is to promote the more efficient teaching of chemistry by modern methods. The choice and arrangement of subject-matter is based on the author's extended experience with students of varied ability. The book as a whole is the outcome of a desire to provide a course in chemistry which shall be a judicious combination of the inductive and deductive methods." Considerable care has been taken to eliminate errors since it appears from the preface that the entire MS. has been read by three other teachers of chemistry and the proof by fourteen.

Laboratory methods are given prominence—there are 201 experiments in all—and the interrogation point is freely used; some teachers will think too freely. Sixteen pages are included in the chapter on acids, bases, and salts and 25 under atoms, molecules, and related subjects. This latter chapter is open to serious criticism. The statements contained in it are well enough, but such topics as the methods for determining atomic weights, ions and ionization and applications of the theory of electrolytic dissociation, are out of place in a first book on chemistry. When teachers of chemistry learn not to give as a first course more than is necessary, and to follow this up by supplementary courses, we shall have better results. Shooting over the heads of students is still the most common fault in textbooks and teachers. The book is an excellent piece of work mechanically.

(2) Like the book noticed above this is evidently intended as a first book in chemistry. The author says: "I have endeavored to provide a book which begins with a course of experimental work for quite young students and develops at the later stages

into a text-book suitable for those who are older ; that is, into a text-book containing fewer facts than those written solely for senior students." Part I contains a concise and well-written introduction treated under the captions: "The Chemistry of Fire; Gain of Weight and Combustion; Lavoisier's Researches on Combustion; Is Matter Indestructible? Can We Create It? and Principle of the Conservation of Mass." These topics are briefly treated and in language easily comprehended by a beginner and are illustrated by experiments to be performed by the student.

Chapters II and III contain an introductory study of water, illustrated by experiments which teach methods of determining melting- and boiling-points, the use of the barometer, fractional and destructive distillation, the pipette, specific gravity determinations, etc. Chapter IV tells how to dissolve, crystallize, the use of plotted curves to show solubility, the desiccator, etc. Chapter V treats of the electrolytic decomposition of water, the chemical elements, compounds and mixtures, synthesis, analysis, substitution, and double decomposition. Chapter VI continues the study of water and treats of water of crystallization, the nature of solution, the action of water with the metals, the composition of water by weight, the law of constant proportions, hydrogen peroxide, and the law of multiple proportions.

Chapter VII is a study of the atmosphere, combustion, flame, plants, and animals.

Part I as outlined above covers 94 pages and contains not a single symbol. In Part II chemical nomenclature is taken up and the rest of the book follows, in great measure, the ordinary line of treatment. Here again too much is given, but in other respects the book is a good piece of work and worth the careful study of teachers.

E. H.

AIR, WATER AND FOOD FROM A SANITARY STANDPOINT. BY ELLEN H. RICHARDS AND ALPHEUS G. WOODMAN. First edition. First thousand. New York: John Wiley & Sons. 1900. 226 pp. Price, \$2.00.

This is an extremely practical book dealing with the common problems of sanitary science in a simple yet thorough manner, and one can not read it through without being convinced that the authors know from their own observations what they are

writing about. After a brief general introduction we find 33 pages devoted to the study of the atmosphere, its general composition, usual contaminations, methods of ventilation, and methods of air analysis from the sanitary standpoint. Then follow, in 78 pages, 3 chapters on water in which many subjects besides those of analysis are discussed. Chapter V is supposed to be written from the "Householder's Standpoint," and Chapter VI from that of the chemist, but both may be read with interest and profit by persons who are not chemists and who have had no training in chemistry beyond that given in ordinary college courses. It is pleasing to see that the authors are not over-impressed with the importance of bacterial analysis in the practical investigations of water. Chapter VII contains a good collection of analytical methods and from the well-known experience of the authors in these matters it will prove valuable to those employed either as teachers of sanitary chemistry or as practical analysts.

The following 75 pages of the book deal with questions of food and partly from the popular standpoint. Many pertinent suggestions are made on the adulteration of common articles, and in the last chapters analytical methods are given by which the practical purity or value of a number of products may be determined. The book closes with a collection of tables, directions for making standard reagents, and with a bibliography of important books and papers dealing especially with topics discussed in the previous pages.

J. H. LONG.

**ESSENTIALS OF MEDICAL AND CLINICAL CHEMISTRY WITH LABORATORY EXERCISES.** BY SAMUEL E. WOODY, A.M., M.D. Fourth edition. Revised and enlarged. Illustrated. Philadelphia: P. Blakiston's Son & Co. 1900. viii+235 pp.

In this book, as in many others of its class, we find an attempt to present what the author considers as the "essentials" of medical chemistry, so-called, within the limits of a single small volume. The space devoted to general and inorganic chemistry, with experiments and qualitative tests, amounts to 124 pages; organic chemistry takes up 47 pages, and clinical chemistry, covering urine analysis and the examination of milk, saliva, and gastric juice, 50 pages more. A very good index completes the book. The author has condensed a good deal of information



(not all of it quite accurate) within the rather narrow limits of the volume and it must be admitted that if the medical student should actually learn all that is there presented he would know much more than the average student carries away with him. But it seems to the present writer that the best selection of matter has not always been made, and that in his effort to be brief the author has very often sacrificed accuracy and clearness. Thus, we find as the definition of an alcohol the following, p. 144: "An alcohol is generally regarded as the hydrate of a hydrocarbon radical, since its formula always has a hydrocarbon radical at its positive end, and the radical HO at the negative end."

It is true that medical students can not devote a large portion of their time to the study of chemistry, but in the time they do spend in elementary chemistry their instruction should be as accurate and systematic as that given to students in the freshman or sophomore years of general colleges. It is a mistake to suppose that there is one kind of elementary chemistry for the clergyman, another for the lawyer, and a third (and the briefest of all) for the doctor. It is the present writer's opinion that the book before him does *not* contain the essentials which a medical man should know.

J. H. LONG.

AN OUTLINE OF THE THEORY OF THERMODYNAMICS. By EDGAR BUCKINGHAM, Associate Professor of Physics and Physical Chemistry in Bryn Mawr College, Bryn Mawr, Pa. xi + 205 pp. New York: The Macmillan Company, 1900. Cloth. Price, \$1.90.

This book is intended to bridge over the gap that exists between the ordinary text-books on thermodynamics and the modern memoirs on the subject. As the title indicates, special stress is laid on the theory, applications being introduced solely for the purpose of illustration. The subject is treated in 13 chapters, the topics considered being: Thermometry, Calorimetry, Material Systems in Thermodynamics, First Law, Principles of Thermochemistry, Calorimetric Properties of Fluids, Second Law, General Equations, Conditions of Thermodynamic Equilibrium, Thermodynamic Potentials, and Free Energy. One chapter is devoted to recapitulation and two to applications, while an appendix contains a list of useful books. The book is also provided with an index.

In treating his subject, the author begins with the explanation of simple fundamental concepts and gradually leads on to the more difficult relations involved; so that the book (though intended to bridge over a gap, as above stated) is yet complete in itself. The presentation is clear; and the student of thermodynamics will find the book a real aid in mastering the subject. The growing importance of thermodynamics in chemistry will insure for this volume a welcome on the part of chemists.

The work of the publishers is excellent.

LOUIS KAHLENBERG.

**THE OIL CHEMISTS' HANDBOOK.** BY ERASTUS HOPKINS, Chemist in charge of the U. S. Laboratories at Boston, Mass. New York: John Wiley & Sons. 8vo. Price, \$3.00.

This book gives, in a clear and concise form, the principal methods of testing the animal and vegetable fats, waxes, and oils, the mineral oils being considered only so far as they occur as adulterants.

A peculiar feature of the work is the tables of the properties and analytical constants of the oils; these have been selected with the greatest care from the original sources, the maximum, minimum, and mean values being given. Their arrangement is numerical; *i. e.*, in the table of the iodine value, the oil having the highest comes first, so with the other constants. These are especially valuable and convenient, as information is obtained at a glance which would take some time to find were it in the body of the book. It is, however, not exclusively a compilation but includes the results of years of practical experience. It seems to the reviewer that in some cases the original method has been adhered to, to the exclusion of the experience of others in the subject. For example the method of Livache is given, as detailed by him in 1886, without stating the experience of Weger and Lippert in 1898 and 1899. So too with regard to the Bechi test, the early procedure employing colza oil (which has since been shown to be unnecessary) is described without giving all the precautions shown to be needful to obtain reliable results; no results of later work are given. Regarding the determination of viscosity it would seem that the statement should have been made that for technical work the Saybolt,

Redwood, or Engler viscosimeter should be employed, rather than a pipette which is no longer much used.

In the matter of references the volume leaves something to be desired, many of the later being omitted, especially in connection with the iodine value. No mention could be found of the heat of bromination test for oils although the valueless sulphur chloride test is given; nor of Halphen's test for cotton-seed oil, one of the most reliable.

There are, too, certain errors of proof-reading and statement which are not in accord with the usual ideas; for example the use of 5.0 instead of 50.0 grams of oil (p 22) for the Maumené test; and in the tables the specific temperature reaction of Gill and Hatch does not refer to the Maumené test but to the heat of bromination test as will be seen from their article.<sup>1</sup> On p. 52. "All good cylinder oils are a mixture of fatty acids and mineral oils;" the cylinder oil should not contain free fatty acids, as most railroad specifications require "acidless animal oil." "Most blown oils are a mixture of fatty acid and mineral oils," being all that is stated about "blown oils," implies that mineral oil is a normal constituent instead of an occasional adulterant.

The tables, however, make the book very valuable and it will doubtless be found very useful to the trade and profession.

AUGUSTUS H. GILL.

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### BOOKS RECEIVED.

**The Oil-Chemists' Handbook.** By Erastus Hopkins, A.M., B.Sc. New York: John Wiley & Sons. 1900. viii + 72 pp. Price, \$3.00.

**The Elements of Inorganic Chemistry, for Use in Schools and Colleges.** By W. A. Shenstone, F.R.S. London: Edward Arnold. 1900. xii + 506 pp. Price, 4s., 6d.

**Experimental Chemistry.** By Lyman C. Newell, Ph.D. Boston: D. C. Heath & Co. 1900. xv + 410 pp.

**Fruit Diseases and How to Treat Them.** Bulletin No. 66. West Virginia Agricultural Experiment Station, Morgantown, W. Va. 38 pp.

**Air, Water, and Food, from a Sanitary Standpoint.** By Ellen H. Richards and Alpheus G. Woodman, Instructors in Sanitary Chemistry in Massachusetts Institute of Technology. New York: John Wiley & Sons; London: Chapman & Hall. 1900. 225 pp. Price, \$2.00.

**The Volatile Oils.** By E. Gildemeister and Fr. Hoffmann. Translated

<sup>1</sup> This Journal, 21, 27.

by Edward Kremers. viii + 733 pp. Four maps and numerous illustrations. 1900. Milwaukee: Pharmaceutical Review Publishing Co. Price, \$5.00 net.

The Wellcome Chemical Research Laboratories, Established 1896. By Frederick B. Power, Ph.D., Director, 6 King St., Snow Hill, London, E. C. 18 pp.

The Question of Temperature-Influence on the Specific Rotation of Sacrose. By Ferdinand G. Wiechmann, Ph.D. 1900. 37 pp.

Nutrition Investigations at the California Agricultural Experiment Station, 1896-1898. By M. E. Jaffa, M.S. Bulletin No. 84. U. S. Department of Agriculture, Washington, D. C. 39 pp.

A Report of Investigations on the Digestibility and Nutritive Value of Bread. By Chas. D. Woods and L. H. Merrill, Maine Agricultural Experiment Station. Bulletin No. 85. U. S. Department of Agriculture, Washington, D. C. 1900. 51 pp.

Commercial Fertilizers. By H. A. Huston, State Chemist, Purdue University, Lafayette, Ind. Special Bulletin. August, 1900. 24 pp. Published by the author.

Elements of Mineralogy, Crystallography, and Blowpipe Analysis, from a Practical Standpoint, including a description of all common or useful minerals, the tests necessary for their identification, the recognition and measurement of their crystals, and a concise statement of their uses in the arts. By Alfred J. Moses, E.M., Ph.D., Professor of Mineralogy, Columbia University, and Charles Lathrop Parsons, B.S., Professor of General and Analytical Chemistry, New Hampshire College. New enlarged edition. viii + 414 pp., with 664 figures. New York: D. Van Nostrand Co. 1900. Price, \$2.00.

The Elements of Physics for Use in High Schools. By Henry Crew, Ph.D., Professor of Physics in Northwestern University. Second Edition, revised. New York: The Macmillan Co. 1900. xvi + 353 pp. Price, \$1.10.

The Laramie Cement Plaster. By E. E. Slosson and R. B. Mondy. Published as part of the Tenth Annual Report of the Wyoming College of Agriculture and Mechanics. Laramie, Wy. 1900. 18 pp.

Alkali Studies, V. By B. C. Buffum and E. E. Slosson. Published as part of the Tenth Annual Report of the Wyoming Experiment Station. Laramie, Wy. July, 1900.

Medical Legislation. Gov. Thomas' Veto of the Colorado Medical Bill. The Love Medical Bill of Ohio. Medical Ethics. Medical Talk Publishing Co., Columbus, Ohio. 16 pp. Price, 5 cents.

Bulletin No. 88. Commercial Fertilizers. August, 1900. 50 pp. Bulletin No. 89. Wheat. September, 1900. 24 pp. Kentucky Agricultural Experiment Station of the State College of Kentucky.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 53.]

THE PRODUCTION OF ALLOYS OF TUNGSTEN AND OF  
MOLYBDENUM IN THE ELECTRIC FURNACE.<sup>1</sup>

BY CHARLES I. SARGENT.

Received September 17, 1900.

INTRODUCTION.

WITH the introduction of the electric furnace, the new field of chemistry at high temperatures was opened to investigation. Moissan especially succeeded in reducing the most refractory oxides, and in volatilizing many of them, as well as certain metals which were considered infusible. He described<sup>2</sup> a method of preparing alloys of vanadium, using the pentoxide as the source of vanadium.

Bernoulli<sup>3</sup> prepared alloys of tungsten with copper, lead, bismuth, cobalt, nickel, etc. His method of working consisted in mixing the oxides of the two metals with lampblack, placing the mixture in a crucible and then heating it in an ordinary furnace. Proceeding in this manner he was not able to obtain alloys containing more than 10 per cent. of tungsten.

<sup>1</sup> From author's thesis presented for the degree of Doctor of Philosophy, University of Pennsylvania, 1900.

<sup>2</sup> "La Four Electrique," p. 246.

<sup>3</sup> Pogg. *Ann.*, 111, 573.

Knowing the comparative ease with which tungsten and molybdenum are reduced from their oxides, it was thought that it might be possible to mix these oxides with oxides of other metals and then reduce the mixture in the electric furnace, obtaining as a final product an alloy of the two metals.

In the following experiments the furnace used was of the type known as the "Moissan." The carbon for the reduction was prepared by ignition of cane-sugar. The crucibles were made of graphite, modeled in the form of an assay scorifier. This shape is preferable, as it allows the arc to play directly on the bottom of the crucible. In some of the experiments the crucibles were lined with magnesia, thus preventing the hot metal from absorbing any of the graphite.

Unless otherwise mentioned the graphite crucibles were used. After each reduction the furnace was closed and allowed to cool before removing the crucible containing the fusion.

Ten preliminary experiments were made with tungstic acid, attention being paid more particularly to the influence of the carbon, and to the variation in voltage and amperage. The results showed that the amount of carbon used exerted a greater influence in the purity of the metal than variations in the strength of current, and the duration of its action. The product invariably contained carbon and traces of unreduced oxide. An effort was made to burn out the carbon by heating the impure metal in magnesia-lined crucibles, but the metal was changed to trioxide and magnesium was volatilized.

#### ALLOYS OF TUNGSTEN.

Tungsten trioxide and bismuthic oxide were mixed in varying amounts with carbon and exposed for several minutes to the action of a current of 60 to 80 volts, and 75 to 150 amperes. The quantity of bismuth detected in the metallic product in no case exceeded 0.64 per cent.

When cupric oxide was substituted for the bismuthic oxide, and a current of 75 to 150 amperes and 60 to 80 volts was applied for five minutes a regulus remained which showed, upon analysis, 18.24 per cent. of tungsten, 77.73 per cent. of copper, and 3.23 per cent. of carbon. On using a crucible lined with magnesia the copper was completely expelled and tungsten trioxide remained.

The results obtained in attempting to prepare an alloy of tungsten and manganese were negative. Two trials were made with chromium with the following conditions:

*Experiment I.—*

2 grams of tungsten trioxide	Voltage, 72–80.
2    "    " chromic oxide	Amperage, 100–160.
2    "    " carbon	Time, 5 minutes.

The reduction was made in a lime crucible. The resulting globule of metal was very hard and brittle, its surface being covered with a layer of chromic oxide. Its interior was gray in color. The specific gravity of the alloy equaled 8.96. It showed, upon analysis, 2.87 per cent. of chromium and 97.64 per cent. of tungsten.

*Experiment II.—*

2 grams of tungsten trioxide	Voltage, 72–85.
2    "    " carbon	Amperage, 100–150.
1 gram of chromic oxide	Time, 5 minutes.

A carbon crucible was used in this experiment, but alloys containing a higher percentage of chromium than given in Experiment I, were not prepared. The next trial was made upon tungsten trioxide and cobaltic oxide with these conditions:

2 grams of tungsten trioxide	Voltage, 70–80.
2    "    " cobaltic oxide	Amperage, 125–150.
1 gram of carbon	Time, 1 minute.

The crucible was of lime and the button, which was strongly magnetic, very tough and tenacious, had the specific gravity 10.96. Its analysis showed 51.86 per cent. of tungsten, and 48.26 per cent. of cobalt.

Upon varying the conditions to

1 gram of tungsten trioxide	Voltage, 65–70,
3 grams of cobaltic oxide	Amperage, 110–130,
2 grams of carbon	Time, 2 minutes,

and using, as before, a lime crucible the resulting metallic globule was discovered to be strongly magnetic, very tough, and it was broken with difficulty. Its specific gravity was found to be 8.92. Its analysis revealed the presence of 29.24 per cent. of tungsten, and 70.10 per cent. of cobalt.

The experiments conducted with the oxides of tungsten and nickel gave very favorable results :

*Experiment I.*

2 grams of tungsten trioxide	Voltage, 68-80.
2    "    " nickel oxide	Amperage, 100-135.
2    "    " carbon	Time, 2 minutes.

The reduction was made in a crucible lined with magnesia, and a globule was obtained which was slightly magnetic, could be filed, and was very tough. Its specific gravity equaled 10.66. Its analysis gave 50.22 per cent. of tungsten, and 49.88 per cent. of nickel.

*Experiment II.—*

3 grams of tungsten trioxide	Voltage, 75-90.
2    "    " carbon	Amperage, 100-175.
1 gram of nickel oxide	Time, 1½ minutes.

The crucible was similar to that used in Experiment I. The resulting button was very hard and non-magnetic, extremely brittle, and easily pulverized. Its specific gravity equaled 12.66. The analysis showed 91.19 per cent. of tungsten, and 8.08 per cent. of nickel.

Repeated attempts were made to alloy tin and tungsten after the plan pursued with the other metals, but without success. It would, therefore, appear that starting with the oxides it is possible to prepare alloys of tungsten with those metals which require a high temperature for their volatilization. In the case of those requiring a low temperature, the oxide is apparently reduced and the metal driven off before the tungstic oxide is reduced. Doubtless alloys of tungsten and the lower fusing metals could be prepared by starting with the metals and melting them together; but if this is attempted in the electric furnace the intense heat drives off the lower-fusing metal, leaving the one with a higher fusing-point in the furnace.

ALLOYS OF MOLYBDENUM.

Three reductions of bismuthic oxide and tungsten trioxide were made :

*Experiment I.—*

4 grams of molybdenum trioxide	Voltage, 65-70.
4    "    " bismuth oxide	Amperage, 90-120.
1 gram of carbon	Time, 2 minutes.



The resulting metal was very hard. Its specific gravity equaled 6.81. It gave, upon analysis, 91.61 per cent. of molybdenum, 6.50 per cent. of bismuth, and 2.28 per cent. of carbon.

*Experiment II.—*

2 grams of molybdenum trioxide	Voltage, 60–70.
8    "    " bismuth oxide	Amperage, 75–110.
1.5   "    " carbon	Time, 2 minutes.

A granular mass was obtained after heating for one and one-half minutes. It was re-fused for one minute in a crucible lined with magnesia, and was converted into a very hard metallic button, having a specific gravity of 8.91. It showed, upon analysis, 92 per cent. of molybdenum, 4.81 per cent. of bismuth, and 3.90 per cent. of carbon.

*Experiment III.—*

6 grams of molybdenum trioxide	Voltage, 70–80.
2    "    " bismuth oxide	Amperage, 100–150.
1 gram of carbon	Time, 2 minutes.

A crucible with magnesia lining was used in this experiment. The analysis showed 97.91 per cent. of molybdenum, 1.10 per cent. of bismuth, and 1.21 per cent. of carbon. All efforts looking to the formation of a molybdenum-copper alloy were fruitless.

In the case of molybdenum and manganese the results were good and entirely unlike those observed with tungsten and manganese, as will be noticed in the following experiments :

*Experiment I.—*

4 grams of molybdenum trioxide	Voltage, 75–85.
4    "    " manganese dioxide	Amperage, 100–150.
3    "    " carbon	Time, 2 minutes.

A button, having a specific gravity of 7.08, was obtained. It gave, upon analysis, 71.07 per cent. of molybdenum, 14.36 per cent. of manganese, 9.60 per cent. of iron, and 4.34 per cent. of carbon. The iron in this alloy came from the manganese dioxide.

*Experiment II.—*

2 grams of molybdenum trioxide	Voltage, 70–80.
6    "    " manganese dioxide	Amperage, 100–130.
3    "    " carbon	Time, 2 minutes.

The resulting alloy had the specific gravity 6.9. Its analysis

revealed the presence of 60.08 per cent. of molybdenum, 21.11 per cent. of manganese, 16.64 per cent. of iron, and 2.99 per cent. of carbon. My experience with molybdenum and chromium is briefly summarized in the following experiments:

*Experiment I.—*

2 grams of molybdenum trioxide	Voltage, 70-90.
6 " " chromic oxide	Amperage, 100-150.
2 " " carbon	Time, 3 minutes.

A carbon crucible was used in the reduction. Molybdenum trioxide, unmixed with carbon, was placed in the bottom of the crucible, and upon this trioxide was introduced a mixture of chromic oxide, the balance of the oxide of molybdenum and carbon. The product of the fusion was hard and brittle. Its specific gravity was found to be 6.53. Its analysis showed the presence of 12.82 per cent. of molybdenum, 76.71 per cent. of chromium, 7.52 per cent. of iron, and 2.55 per cent. of carbon.

*Experiment II.—*

4 grams of molybdenum trioxide	Voltage, 70-80.
4 " " chromic oxide	Amperage, 90-130.
3 " " carbon	Time, 3 minutes.

The alloy, steel-gray in color, proved to be hard and brittle. Its specific gravity was found to be 7.65, and upon analysis it showed 39.96 per cent. of molybdenum, 53.24 per cent. of chromium, and 6.22 per cent. of iron with a trace of carbon. An alloy of tin and molybdenum was not obtained.

Several trials were made with molybdenum and nickel oxides, but only those will be introduced here which gave definite results:

*Experiment I.—*

2 grams of molybdenum trioxide	Voltage, 70-80.
4 " " nickel oxide	Amperage, 75-125.
2 " " carbon	Time, 2 minutes.

The crucible was lined with magnesia for this fusion. The metal obtained was very hard and brittle, non-magnetic, and had a specific gravity of 7.61. Upon analysis it gave 17.72 per cent. of molybdenum, 80.93 per cent. of nickel, and 1.63 per cent. of carbon.

*Experiment II.—*

4 grams of molybdenum trioxide	Voltage, 75–80.
2 “ “ nickel oxide	Amperage, 100–150.
2 “ “ carbon	Time, 1 minute.

The alloy was soft and easily filed. It was non-magnetic and its specific gravity was found to be 8.00. Its analysis showed 65.10 per cent. of molybdenum, and 34.72 per cent. of nickel.

*Experiment III.—*

4 grams of molybdenum trioxide	Voltage, 73–75.
2 “ “ nickel oxide	Amperage, 140–160.
2 “ “ carbon	Time, 1 minute.

A graphite crucible was used in the reduction. The alloy was hard, brittle, and non-magnetic. Its specific gravity equaled 8.88. Its analysis showed the presence of 50.20 per cent. of nickel, 42.48 per cent. of molybdenum, 3.05 per cent. of carbon, and 4.04 per cent. of silica. The silica probably came from the material used in the manufacture of the graphite crucible.

The reduction of mixed oxides of molybdenum and cobalt was not attended with the least difficulty; indeed, from the appended results it would seem that these particular metals alloy in almost any proportion:

*Experiment I.—*

2 grams of molybdenum trioxide	Voltage, 68–75.
4 “ “ cobaltic oxide	Amperage, 100–175.
2 “ “ carbon	Time, 1½ minutes.

The crucible had a magnesia lining. The alloy was very hard, tough, and magnetic. Its specific gravity equaled 7.32. Its analysis gave 17.06 per cent. of molybdenum, and 82.34 per cent. of cobalt.

*Experiment II.—*

3 grams of molybdenum trioxide	Voltage, 70–90.
3 “ “ cobaltic oxide	Amperage, 100–160.
2 “ “ carbon	Time, 1½ minutes.

The crucible was lined with magnesia. The alloy was very hard, tough, and magnetic. Its specific gravity equaled 6.44. Its analysis showed 35.64 per cent. of molybdenum, 62.91 per cent. of cobalt, and 1.79 per cent. of carbon.

*Experiment III.—*

3 grams of molybdenum trioxide	Voltage, 75–80.
3    "    " cobaltic oxide	Amperage, 175–190.
2    "    " carbon	Time, 1½ minutes.

In this experiment I used a graphite crucible, and obtained an alloy that was hard, slightly magnetic, very brittle, and easily pulverized. The specific gravity was 6.94. Its analysis gave 47.10 per cent. of molybdenum, and 52.30 per cent. of cobalt.

*Experiment IV.—*

4 grams of molybdenum trioxide	Voltage, 75–95.
2    "    " cobaltic oxide	Amperage, 125–175.
2    "    " carbon	Time, 1½ minutes.

The crucible was lined with magnesia. The alloy was very hard, brittle, and feebly magnetic, with a specific gravity of 7.14. Its analysis gave 54.57 per cent. of molybdenum, and 45.35 per cent. of cobalt.

*Experiment V.—*

4 grams of molybdenum trioxide	Voltage, 70–100.
2    "    " cobaltic oxide	Amperage, 110–150.
2    "    " carbon	Time, 1½ minutes.

Here I used a graphite crucible, placing the molybdic oxide in the bottom. The alloy was soft enough to be filed, but was brittle and slightly magnetic. The specific gravity was 6.55. It gave, upon analysis, 49.47 per cent. of molybdenum, and 50.86 per cent. of cobalt.

While tungsten and molybdenum ordinarily show many similarities in their reactions, we observe in the preceding experiments differences not wholly devoid of interest. Thus, while tungsten and bismuth did not yield an alloy, with molybdenum and bismuth definite products did result. The experiments with tungsten and copper were positive, but with molybdenum it seemed impossible to alloy copper. Both metals failed to unite with tin, and while this was true of tungsten with manganese, the latter metal and molybdenum combined with apparent readiness. Cobalt, chromium, and nickel, of the seven metals whose oxides were used with the oxides of tungsten and molybdenum, seemed to alloy with the greatest ease with the tungsten and

molybdenum, yielding products which, in the case of cobalt and nickel, may prove to possess a commercial technical value, if prepared in large amounts.

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## A METHOD FOR THE RAPID DETERMINATION OF CARBON IN STEEL.

BY ROBERT JOB AND CHARLES T. DAVIES.

Received September 25, 1900.

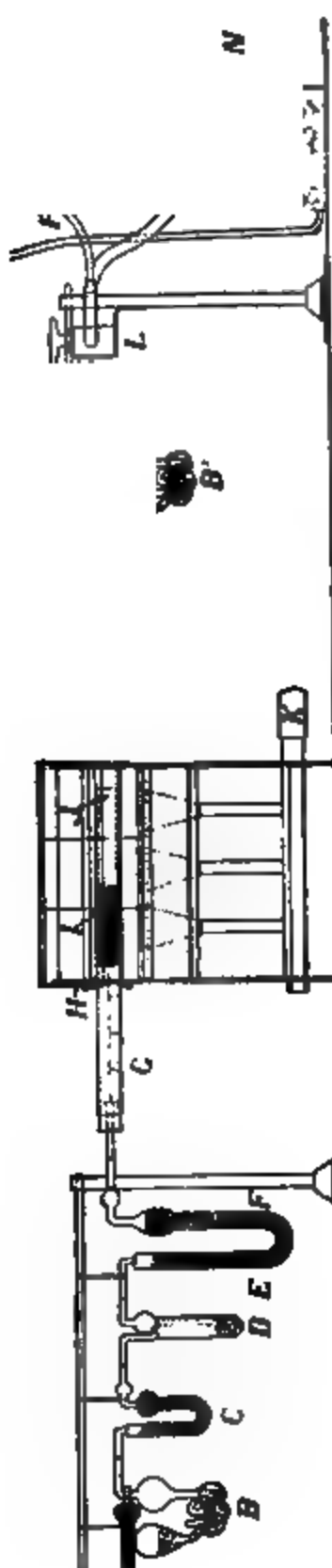
**A**FTER a very thorough trial of Dr. Sargent's apparatus for the rapid determination of carbon,<sup>1</sup> an investigation was begun with the object of retaining the continuous heating arrangement, and of reducing the apparatus to the simplest possible form without impairing in any way the accuracy of the results.

At the outset it was found that the separate, water-jacketed, copper oxide tube could be entirely eliminated by simply increasing the length of the combustion furnace to 9 inches, increasing the length of the porcelain combustion tube to 20 inches, and inserting closely rolled copper gauze about 4 inches in length, thoroughly oxidized prior to use, into the combustion tube, exactly as in the old method, placing pieces of clay-pipe stems between the copper oxide and the end of the tube in order to prevent the former from being forced out of place when the boat was run up against it in the determination.

Experiments with the furnace itself showed that three Bunsen burners each about  $2\frac{1}{4}$  inches apart, having spreaders upon the tops, furnished sufficient heat to keep the porcelain tube at a bright red heat over 8 inches of its length. A thin sheet-iron shield was placed just beneath the tube as a protection from the direct action of the flame.

After the removal of the separate copper oxide tube, it was found that the gases, upon reaching the calcium chloride tube preceding the weighed bulbs, had been cooled to the temperature of the room, so that the condensing worm was no longer necessary, and further test after its removal proved that the excess of water remaining in the gas at that point was small, and was readily removed by the calcium chloride without necessity of frequent changing. It was further proved that the absorption

<sup>1</sup> This Journal, 22, 277.



of carbon dioxide in the bulbs was complete under these conditions, and that the temperature of the solution in the latter was not perceptibly raised, even upon very rapid running,—and also that moisture did not escape from the weighed potash bulbs and attached calcium chloride tube, even when the air was run at the rate of 8 bubbles per second, or faster than necessary to complete the combustion in twenty minutes.

Attention was next directed to the sand tube for the removal of chlorine and hydrochloric acid. Under certain conditions, and especially in very warm weather, it was found that the absorption by moist sand was incomplete, and thus that uniformly correct results could not be depended upon with this arrangement. Careful trial was therefore made of various absorbents both wet and dry, and we finally adopted the anhydrous cupric sulphate and cuprous chloride U-tube recommended by Blair, inserting beyond it a small bubble tube containing about 10 cc. of a saturated solution of silver sulphate in sulphuric acid of 1.40 specific gravity which served the double purpose of retaining any hydrochloric acid which might pass the U-tube, and of remedy-

ing the excessive dehydration produced by the copper salts.

The U-tube, E,F, is of the ordinary 6 inch form, and when filled contains cupric sulphate in the arm F, and cuprous chloride in E, both salts being freshly and thoroughly dehydrated, the copper sulphate being nearly white, and the cuprous chloride a dull brown. A small piece of glass wool is placed at the bottom of the tube to separate the salts, and also upon the top. The materials should be in granular form about  $\frac{1}{8}$  inch in diameter, free from powder.

After once filling the tube it may be safely used without change until the copper sulphate on the top of the arm F becomes slightly blue or green, or until traces of hydrochloric acid begin to be caught in the silver sulphate solution. The tube should then be removed, placed upon the steam table, or otherwise heated, and a slow suction applied until the cupric sulphate has become nearly white. A second U-tube is kept on hand ready for use and is inserted while the other is being dehydrated. Heating and aspirating for an hour will generally produce the proper dehydration, and the tube is then capped and hung up ready for use. As a general thing a large number of determinations may be made without changing the tube.

The silver sulphate bubble tube, D, is about  $4\frac{3}{4}$  inches in height, and  $\frac{7}{8}$  inch in diameter, holding about 25 cc., if full. When in use the tube contains from 5 to 10 cc. of the silver sulphate solution, this being blown in from a small wash-bottle. The tube is refilled after a determination if any precipitate has formed. This, however, seldom occurs unless the copper salts have become partially hydrated.

The calcium chloride tube, C, next to the silver sulphate tube retains the excess of moisture from the latter, and the gas passes into the potash bulbs in precisely the same degree of dryness as it emerges from the calcium chloride tube attached to the weighed bulbs, as shown by the fact that in the blank determinations there is almost invariably neither loss nor gain in the weight of the bulbs.

In filling the calcium chloride tubes care should be taken that the material be freshly dehydrated, and in granular pieces about  $\frac{1}{8}$  inch in diameter and free from dust. The tubes should be filled as completely as possible, tapping lightly upon them and

filling close to the top, placing a very small piece of cotton at each end.

The potash bulbs, B and B', are practically the same as those recommended by Dr. Sargent, and hold, when filled for use, about 35 cc. of potassium hydroxide and weigh, including the calcium chloride, about 80 grams. These bulbs may be safely used until they have absorbed 2.5 grams carbon dioxide after which they should be cleaned out and refilled with fresh potash solution of 1.27 specific gravity. The calcium chloride tube, which is about  $2\frac{3}{4}$  inches in length, and  $\frac{1}{4}$  inch in diameter, should also be refilled with dehydrated material at the same time. The calcium chloride tube, C, immediately before the weighed bulbs, should be refilled in the same manner as soon as the material begins to appear slightly moist at the end nearest the silver sulphate tube. This will usually occur after about fifty determinations. The old calcium chloride when removed can be thoroughly dehydrated in a few minutes by heating in an iron or porcelain dish.

In the course of our work more or less difficulty was at first experienced owing to the cracking of the porcelain tube, especially so when the boats were not warmed before inserting. We found, however, that this could be completely remedied by putting into the combustion tube a piece of platinum foil bent into tubular form, and fitting the combustion tube closely, being careful to have the edges somewhat beveled so that the boat, when pushed in with the wire, would run up smoothly upon the foil, the object of the latter, being, of course, to withdraw the heat absorbed by the boat from a considerable area of the combustion tube instead of from a few points. The above was noted by Dr. Sargent in the paper above referred to.

Attention was next turned to the purity of the oxygen supply, in order to avoid the necessity for the preheating furnace. Investigation showed that commercial oxygen free from hydrocarbons could be readily obtained. Therefore, we merely stipulate with the order that the material shall be of this quality, and upon arrival of the tank run a blank determination, passing the oxygen for ten minutes and then the air in the usual manner. The final weight of the bulbs after forty minutes in the balance should not vary more than 0.2 of a milligram from the original weight. In case, however, a pure supply could not be obtained,



thus necessitating preheating of the gas, we found that a separate appliance could be avoided by simply passing a copper tube through the combustion furnace, utilizing the heat of the 3 burners for the purpose. An apparatus of this nature was attached readily to the furnace by boring two quarter-inch holes in each end of the furnace just above, and slightly to one side of the spreaders of the Bunsen burners, running a seamless copper tube of  $\frac{1}{4}$  inch outside diameter entirely through the furnace, out through the end and back upon the opposite side parallel to the first, having the tube in such position that the flame would not play directly upon it, but still so close that the heat would bring it to redness. The ends of this tube, after passing through the furnace, were bent down almost to the level of the desk, and then extended along to the connection of the oxygen supply beyond the three-way cock, L. With this length of about 18 inches from the furnace, the ends of the copper remained cool under all conditions of service, and could thus be attached direct to the rubber tubes leading respectively to the oxygen and to the three-way cock, without any necessity for a water-cooling arrangement.

In the regular determinations we heat up the furnace by lighting the middle burner, turning up one-half for five minutes, then turning up full, at the same time turning up the two end burners one-half, and after five minutes giving the full flame. The tube will be red hot within fifteen minutes from the start, and ready for the day's determinations. If then a boat is in the tube it is pulled out with the wire hook quickly upon a porcelain tile, the weighed potash bulbs, after removing the capillary tips, are connected in position, and the oxygen started through the purifying bulbs, B', at the rate of about 4 bubbles per second. The determination boat is then removed from the oven, placed within the end of the tube and run quickly into position against the copper oxide with the wire, which is removed at once, and the gum stopper inserted. The oxygen is passed for seven minutes at the above rate, then shut off, and the three-way cock turned and air passed at the rate of about 6 or 7 bubbles per second for twelve and one-half minutes regulating the pressure as necessary by means of the clamp O, and passing about 1 liter of air. The stopper is then removed from the end of the tube,

the bulbs disconnected, and another set of previously weighed bulbs inserted and the second combustion proceeded with. Three weighed bulbs are used in running a set of determinations, and one of the same size but slightly lighter than the others is kept upon the opposite pan of the balances as a counterpoise. The weights are taken after letting the bulbs stand for forty minutes in the balances. The furnace remains hot throughout the day's work without attention.

As to accuracy of results with this apparatus, we have checked repeatedly upon various standard steels, and have obtained uniform and practically identical results with those obtained by the regular combustion method with a platinum tube.

In its present form the apparatus can be readily made by cutting down an old furnace; no water connections are required, the number of joints is reduced to a minimum, the cost of operation as well as the initial cost are greatly reduced below the cost of the old combustion method, a porcelain tube is as satisfactory and quick as a platinum tube, and the entire apparatus from end to end can be placed upon a table 5 feet long.

In this apparatus we have retained what seemed to be for our purpose the most desirable features of the various appliances now in use and wish to make due acknowledgment for them.<sup>1</sup>

We have found it very advantageous to rechlorinate the double chloride of copper and potassium solution after Dr. Sargent's method.<sup>2</sup> As the solution gradually becomes neutral we find it desirable after rechlorinating to make addition of hydrochloric acid in sufficient amount to restore the original acidity, thus preventing the separation of salts, and increasing the rapidity of solution.

The acidity can be determined very easily by titrating 5 cc. of the rechlorinated solution with standard potassium hydroxide solution, taking as the end-reaction the point at which the ferric hydroxide just formed fails to go into solution after shaking. Titration is then made of 5 cc. of a solution of one part hydrochloric acid and 13 parts water (the normal acidity of the double chloride solution) with a drop of neutral ferric salt as indicator, the end-point being determined as above; comparison of the

<sup>1</sup> The potash bulbs and silver sulphate tube were made to order by Queen & Co.

<sup>2</sup> This Journal, 22, 210.

acidity of the two solutions with the volume of the solution rechlorinated will show the amount of hydrochloric acid needed.

LABORATORY OF THE PHILADELPHIA AND READING  
RAILWAY COMPANY, READING, PA.,  
September 13, 1900.

## DETERMINATION OF IRON IN MAGNETITE ORE BY THE SPECIFIC GRAVITY TEST.<sup>1</sup>

BY JOSEPH W. RICHARDS.

Received October 22, 1900.

**M**ANY magnetite ores are simply mixtures of magnetite and quartz. The dressing of such ores at the mines up to a salable percentage of iron is often an important matter, and in such cases the weight of the ore, as determined by its "feel," is the determining factor as to whether it should pass into the ore pile or to the dump. Every new streak of ore opened up brings new material to be thus classified. For such classification, the specific gravity of the ore, carefully taken on a good pair of scales, is of quite sufficient accuracy to answer all practical purposes. Indeed, in many cases, considering the difficulty of obtaining a small representative sample from a mixed lot of ore such as the chemist requires, the specific gravity test made on a considerable weight of sample pieces may be quite as satisfactory as an analysis. The various ways in which specific gravity may be practically determined on an ordinary good scale need not be discussed here; anywhere from 1 to 50 pounds of ore may be tested, according to the scale at hand, and the accuracy desired, and results usually obtained accurate to 0.10 in any case, and often to 0.02 or 0.03, in the specific gravity. Such variations would mean a variation of 1 to 3 per cent. on the iron content, according to the richness of the ore. With ores over 45 per cent. of iron, the variation or error need not be over 2 per cent. on the iron, in any case.

To facilitate such tests, I have calculated the following table of the specific gravity of mixtures of magnetite and silica, of specific gravity of 5.18, and 2.66 respectively, for every 1 per cent. of iron contained, giving in each case also the percentages of magnetite and quartz in the mixture, the latter datum being of particular importance in valuing the ore.

<sup>1</sup> Read at the October meeting of the Lehigh Valley Section of the American Chemical Society.

Fe. Per cent.	Fe <sub>2</sub> O <sub>4</sub> . Per cent.	SiO <sub>2</sub> . Per cent.	Specific gravity.	Fe. Per cent.	Fe <sub>2</sub> O <sub>4</sub> . Per cent.	SiO <sub>2</sub> . Per cent.	Specific gravity.
0	0.0	100.0	2.66	37	51.0	49.0	3.54
1	1.4	98.6	2.67	38	52.4	47.6	3.57
2	2.8	97.2	2.69	39	53.8	46.2	3.60
3	4.1	95.9	2.71	40	55.2	44.8	3.64
4	5.5	94.5	2.73	41	56.6	43.4	3.67
5	6.9	93.1	2.75	42	58.0	42.0	3.70
6	8.3	91.7	2.77	43	59.4	40.6	3.74
7	9.7	90.3	2.79	44	60.8	39.2	3.77
8	11.0	89.0	2.81	45	62.1	37.9	3.81
9	12.4	87.6	2.83	46	63.5	36.5	3.85
10	13.8	86.2	2.85	47	64.9	35.1	3.89
11	15.2	84.8	2.87	48	66.3	33.7	3.93
12	16.6	83.4	2.89	49	67.7	32.3	3.97
13	18.0	82.0	2.92	50	69.1	30.9	4.01
14	19.3	80.7	2.94	51	70.5	29.5	4.05
15	20.7	79.3	2.96	52	71.8	28.2	4.09
16	22.1	77.9	2.98	53	73.2	26.8	4.13
17	23.5	76.5	3.00	54	74.6	25.4	4.17
18	24.8	75.2	3.03	55	76.0	24.0	4.22
19	26.2	73.8	3.05	56	77.4	22.6	4.26
20	27.6	72.4	3.07	57	78.8	21.2	4.31
21	29.0	71.0	3.09	58	80.1	19.9	4.36
22	30.4	69.6	3.12	59	81.5	18.5	4.41
23	31.8	68.2	3.14	60	82.9	17.1	4.46
24	33.2	66.8	3.17	61	84.2	15.8	4.51
25	34.5	65.5	3.20	62	85.6	14.4	4.56
26	35.9	64.1	3.22	63	87.0	13.0	4.61
27	37.3	62.7	3.25	64	88.4	11.6	4.66
28	38.7	61.3	3.27	65	89.8	10.2	4.72
29	40.0	60.0	3.30	66	91.2	9.8	4.78
30	41.4	58.5	3.33	67	92.6	7.4	4.84
31	42.8	57.2	3.36	68	94.0	6.0	4.90
32	44.2	55.8	3.39	69	95.3	4.7	4.96
33	45.6	54.4	3.42	70	96.7	3.4	5.02
34	47.0	53.0	3.45	71	98.0	2.0	5.09
35	48.3	51.7	3.48	72	99.4	0.6	5.16
36	49.7	50.3	3.51	72.4	100.0	0.0	5.18

LEHIGH UNIVERSITY,  
October 18, 1900.

IRREGULAR DISTRIBUTION OF SULPHUR IN PIG IRON.

BY RANDOLPH BOLLING.

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SULPHUR determinations sometimes show marked differences when samples are drilled from different points on the same pig. M. J. Moore<sup>1</sup> has noticed the low results obtained from

<sup>1</sup> This Journal, 21, 972-975.

“shot samples” as compared with those cast in sand. He states that the results obtained from the “shot samples” are low as compared with the gravimetric determinations. Moore used the volumetric method on his sand and shot samples.

The variations between sulphur determinations, made on drillings from the lower surface of the pig, and those made on the upper surface have been frequently noticed here, and in some cases have been so marked that a cast which was drilled from the top surface of the sample pig, on analysis, showed 0.075 per cent. sulphur, and consequently graded as “off basic” (sulphur running over 0.05 per cent.) was found to be “basic” when the drillings were taken by drilling a hole entirely through the pig; the second determination showed 0.045 per cent. sulphur.

To study the irregular distribution of sulphur a rod  $12 \times 14$  inches was cast in sand by collecting a pound or so at intervals from the runner as a cast was being made until about 10 pounds had been ladled out, and then poured into the mold. This was then drilled at regular intervals of  $1\frac{5}{8}$  inches; in all 8 holes were drilled. Sulphur was determined by the cadmium chloride method. The figure represents a cross-section of the rod reduced to a small scale. Beginning at bottom of the rod at the point marked A, the decimal points will indicate where the drill entered. The percentages of sulphur it will be noticed are lower at the bottom of the mold than at the top.

.036
.036
.036
.036
.036
.032
.03
.023
A

It will be seen that the difference between the upper and lower surface amounts to 0.013 per cent., and it would therefore be wrong to report a determination made on drillings taken either at the top or bottom; and to obtain a representative sample it would be necessary to drill a hole entirely through the sample pig, and mix the drillings well before making the determination. By this procedure a fairly average sample would be obtained.

[CONTRIBUTION FROM THE CHEMICAL DIVISION, U. S. DEPARTMENT OF AGRICULTURE, No. 39. SENT BY H. W. WILEY.]

## THE COMPOSITION AND ANALYSIS OF LONDON PURPLE

BY J. K. HAYWOOD.

Received October 22, 1900.

LONDON purple has, up to the present time, been supposed to consist mainly of calcium arsenite and an organic dye residue. From the work which will appear later on in this article, however, it is shown that the arsenic in London purple is principally in the "ic" condition, so that it consists mainly of calcium arsenate, calcium arsenite, and an organic dye residue. On account of the method of manufacture, as I have mentioned in an earlier paper,<sup>1</sup> some of the arsenic will nearly, or quite, always appear in the free condition. It will thus be seen that an analysis of London purple would include the determination of moisture, total arsenic acid, total arsenious acid, soluble arsenic acid, soluble arsenious acid, calcium, and sand.

### DETERMINATION OF MOISTURE.

The moisture of London purple, was determined by drying at 100° for from twelve to fifteen hours. On four samples (A, B, C, and D) examined by me the results were :

	A.	B.	C.	D.
	Per cent.	Per cent.	Per cent.	Per cent.
Moisture .....	1.87	4.07	2.76	2.73

### DETERMINATION OF TOTAL ARSENIC.

As regards the determination of total arsenic, it will at once be seen that on account of the presence of the organic dye-stuff residue, and of the calcium, the same methods cannot be applied as those mentioned in my earlier paper for Paris and Scheele greens.

I therefore tried to apply to London purple the same method for determining total arsenic as is used for determining phosphoric acid in phosphates, namely :

1. About 0.5 gram of the sample was oxidized with fuming nitric acid, the excess removed by evaporation, molybdate

<sup>1</sup> "Adulteration and Analysis of the Arsenical Insecticides." This Journal, 22, 528

solution added and the yellow precipitate carefully washed, and afterwards dissolved in ammonia, magnesium mixture added and the arsenious oxide weighed as magnesium pyroarsenate ( $\text{Mg}_2\text{As}_2\text{O}_7$ ). In carrying out this method, however, I found that the fuming nitric acid did not oxidize all of the organic dye-stuff and that consequently all of the yellow molybdate precipitate did not come down. As the results obtained showed that the amount of arsenious oxide was about 10 per cent. below that which I subsequently found to be present, the method was abandoned.

2. I next tried to determine the total arsenic by dissolving the purple in hydrochloric acid, precipitating with hydrogen sulphide, washing, dissolving in ammonia, reprecipitating with hydrochloric acid, washing first with water, then, after drying, with carbon disulphide, and finally weighing as arsenious sulphide. The arsenious sulphide obtained, however, was perfectly black, from contamination with organic matter, hence this method was also abandoned.

3. The next method which I tried was as follows:

About 2 grams of the sample were dissolved in hydrochloric acid (1 : 4) and heated to from  $60^\circ$ – $70^\circ$  C. to get all arsenic in solution (not higher for fear of driving off arsenious chloride). The solution was then filtered to a definite volume, an aliquot portion taken for analysis and the arsenic precipitated by hydrogen sulphide at  $70^\circ$  C. The precipitate was separated by filtration, washed, and finally both filter and precipitate oxidized with fuming nitric acid in a small flask. After all sulphur and organic matter appeared to be oxidized, the solution was evaporated to a small volume, filtered, treated with magnesia mixture prepared according to the Austin formula,<sup>1</sup> and then with a little ammonia. After settling a few hours the precipitate was washed with ammonia water (1 cc. ammonia to 100 cc. of water) on a Gooch crucible, dried, and the Gooch crucible placed in a solid platinum crucible where it was ignited by degrees in the ordinary way.

Employing this method, the following results were obtained on the four samples (A, B, C, and D) :

<sup>1</sup> *Ztschr. anorg. Chem.*, 23, Heft. 2.

	A.	B.	C.	D.
	Per cent.	Per cent.	Per cent.	Per cent.
Arsenious oxide.....	35.50	37.48	36.47	35.90

Another sample, X, gave results in triplicate, as follows:

Per cent.

33.53

33.32

33.79

Although this method seemed to give fairly good results, I did not feel satisfied for two reasons, namely:

1. The magnesium ammonium arsenate was always dark-colored, showing that the nitric acid had not oxidized all the organic matter, and that consequently when the precipitate was ignited, there would be a loss of arsenic.

2. From the length of time necessary to precipitate the arsenious sulphide ( $\text{As}_2\text{S}_3$ ), it appeared to me that some of it at any rate must be in the "ic" condition, and that consequently a method should be employed which would differentiate between the "ous" and "ic" arsenic.

With these two points in view I worked out a method modeled after the Thorn Smith method, mentioned in my earlier paper, but quite different in all of the small details. It is as follows:

3. Two grams of London purple were dissolved in about 80 cc. of water, and 20 cc. of hydrochloric acid at a temperature of from  $60^\circ$  to  $70^\circ$ , just as in the method above described, filtered, and washed to a volume of 300 cc. One hundred cc. of this was treated in a 500 cc. flask with sodium bicarbonate in excess. The contents of the flask were then brought to the mark with water, using a few drops of ether to destroy bubbles, and 250 cc. filtered off. To this was added starch solution, and the standard iodine solution, until the blue color appeared. The result was the arsenious oxide as such, in 50 cc. of the original solution.

Again 50 cc. of the original solution (representing 0.3333 gram) was heated to  $80^\circ$  on the water-bath, and then taken off and 50 cc. of hydrochloric acid, and three grams of potassium iodide added. The mixture was allowed to stand for at least fifteen minutes, the "ic" arsenic thus being reduced to "ous" arsenic by the action of the potassium iodide, in the acid solution,



iodine being set free. The solution was then rinsed out in a large beaker, and tenth-normal sodium thiosulphate added, drop by drop, to get rid of the iodine. The end-point here was rather difficult to read on account of the very dark color of the solution, but with a little practice one could determine it very easily, by proceeding as follows :

The sodium thiosulphate was run in a little at a time and occasionally a drop of the solution was added to a drop of starch paste. This would of course give a blue color with the starch, which became fainter and fainter as the iodine was used up. Finally when a drop of the solution only gave the slightest blue color, with the starch, a little starch paste was added directly to the whole solution, and the blue color dissipated with a few drops of thiosulphate. With a little practice one could in this way get the exact end-point every time. The solution was immediately made alkaline with solid sodium carbonate. It was again made slightly acid with hydrochloric acid, taking care that all of the solid particles of the sodium carbonate on the bottom were neutralized by the acid,<sup>1</sup> and finally made alkaline with sodium bicarbonate. Starch paste was now added and tenth-normal iodine until the blue color appeared. This end-point is easily read if the beaker is placed on a white surface between the eye and the light, and iodine run in until a distinct purple color appears. The figure thus obtained gave the total amount of arsenic in the solution as arsenious oxide. Subtracting the first figure from this we have the amount of arsenious oxide corresponding to arsenic oxide in 50 cc. of the original liquid. Working in this way I obtained the following results on the samples (A, B, C, and D).

Sample.	Arsenious oxide as such. Per cent.	Total arsenious oxide present. Per cent.	Arsenious oxide corresponding to arsenic oxide. Per cent.	Arsenic oxide present. Per cent.
A .....	8.16	37.21	29.05	33.77
	8.16	37.21	29.05	33.77
	...	36.78	28.62	33.26

<sup>1</sup> If all of the sodium carbonate is not used up, it will itself act on the standard iodine subsequently to be added.

Sample.	Arsenious oxide as such. Per cent.	Total arsenious oxide present. Per cent.	Arsenious oxide corresponding to arsenic oxide. Per cent.	Arsenic oxide present. Per cent.
B .....	17.45	39.97	22.67	26.34
	17.16	40.12	22.82	26.50
	....	40.26	22.96	26.66
C .....	10.47	38.67	28.20	32.76
	10.47	38.81	28.34	32.93
D .....	6.40	37.07	30.67	35.62
	6.40	36.92	30.52	35.45
	...	37.21	30.81	35.79

It will thus be seen that this method not only allows of a determination of the arsenious oxide and the arsenic oxide but also gives very good duplicate results, which results are higher than those obtained by the previous methods. One would expect this on account of the loss which very likely takes place in the last method when the magnesium ammonium arsenate is burned in the presence of some organic matter, which has not been removed by the fuming nitric acid.

DETERMINATION OF CALCIUM OXIDE.

In order to determine calcium oxide in London purple, a portion was dissolved in hydrochloric acid (an aliquot portion of the 300 cc. used in the determination of arsenious and arsenic oxides above would do), and hydrogen sulphide passed through. The precipitate was well washed, the filtrate evaporated to small bulk and transferred to a 200 cc. flask, when it was treated with ammonia (to precipitate the iron, etc.) and made to the mark. A 100 cc. portion of this was filtered off and treated with ammonium oxalate in the usual way. In this manner the following results were obtained on the samples (A, B, C, and D).

Samples.	Calcium oxide. Per cent.
A .....	25.09
B .....	23.59
C .....	24.55
D .....	25.03
On a fifth sample, X, triplicate results were..	{ 23.25 23.25 23.40

DETERMINATION OF SOLUBLE ARSENIOS OXIDE.

To determine the soluble arsenious oxide, the same methods were used as those described in my previous paper for Paris and Scheele greens.<sup>1</sup> On a fifth sample, X, the results were as follows :

Method 1. Washing on the filter not tried.

Method 2. Extracting 1 gram with 500 cc. of water for a number of days at room temperature, and determining arsenious oxide by standard iodine in an aliquot portion of the filtrate.

Sample.	Time.	Arsenious oxide extracted. Per cent.
X.....	5 days	7.29
	10 days	7.88
	19 days	7.88

Method 3. Extracting 1 gram with successive portions of water at 50°-60° C.

Time.	Arsenious oxide extracted. Per cent.
1 day.....	7.78
2 days.....	7.78 + 1.65 = 9.43
3 days.....	9.43 + 0.87 = 10.30
4 days.....	10.30 + 0.49 = 10.79
5 days.....	10.79 + 0.39 = 11.18
6 days.....	11.18 + 0.29 = 11.47
7 days.....	11.47 + 0.19 = 11.66
8 days.....	11.66 + 0.24 = 11.90
9 days.....	Still gaining.

It will be seen from this that the only method which gave constant results was Method 2, above, just as in the case of Paris and Scheele greens. Applying this method to Samples A, B, C, and D, the following results were obtained :

Sample Nos.	Soluble arsenious oxide. Per cent.
A .....	2.43
B .....	13.3
	13.60
C .....	3.88
D .....	1.44

DETERMINATION OF SOLUBLE ARSENIC OXIDE.

To determine the soluble arsenic oxide, an aliquot portion of

<sup>1</sup> "Adulteration and Analysis of the Arsenical Insecticides." This Journal, 22, 568.

the liquid from Method 2 above, for soluble arsenious oxide (say 200 cc.), was transferred to a flask, made slightly alkaline with NaOH, and evaporated to about 25 cc. on a hot plate. The flask was then removed and allowed to cool to about 80°, and an equal volume of concentrated hydrochloric acid and 3 grams of potassium iodide added. It was allowed to stand fifteen minutes, the iodine set free, exactly used up with tenth-normal thiosulphate (the end-point is easily read without the use of starch), and the solution neutralized with sodium carbonate. It was again made slightly acid with hydrochloric acid, taking care that all lumps of sodium carbonate were acted on, then made alkaline with an excess of sodium bicarbonate, and titrated with iodine, using starch as an indicator. From this figure was subtracted the figure representing the amount of soluble arsenious oxide, and the remainder was calculated as arsenic oxide.

Proceeding in this way I obtained the following results:

Sample.	Soluble arsenic oxide. Per cent.
A .....	15.81
B .....	7.12
C .....	12.56
D .....	19.56

#### DETERMINATION OF SOLUBLE CALCIUM OXIDE.

In Method 2 above for soluble arsenious oxide and arsenic oxide, I also determined the per cent. of calcium oxide that had been dissolved by the action of the 500 cc. of water. The results on the samples (A, B, C and D) were as follows:

Sample.	Calcium oxide dis- solved by 500 cc. of water. Per cent.
A .....	7.80
B .....	6.60
C .....	7.00
D .....	10.80

#### DETERMINATION OF OTHER INORGANIC MATTERS.

The inorganic matter, insoluble in hydrochloric acid, mostly consisting of sand, was determined by dissolving the London purple in hydrochloric acid, filtering, washing, and burning the

filter and contents. The results obtained on the samples (A, B, C and D) were as follows :

Sample.	Sand. Per cent.
A .....	3.54
B.....	2.61
C .....	2.46
D .....	3.55

The following is a condensed statement of the work done :

Sample.	Water. Per cent.	Sand. Per cent.	Total arsenic <sup>1</sup> cal- culated as As <sub>2</sub> O <sub>3</sub> .		Total arsenious oxide as such. Per cent.	Total arsenic ox- ide as such. Per cent.	Total calcium oxide. Per cent.
			Precipitating as arsenious sul- phide, oxidizing with nitric acid. (3) Per cent.	Volumetric io- dine method. (4) Per cent.			
A .....	1.87	3.54	35.50	37.07	8.16	33.60	25.09
B .....	4.07	2.61	37.48	40.12	17.31	26.50	23.59
C .....	2.76	2.46	36.47	38.74	10.47	32.84	24.55
D .....	2.73	3.55	35.90	37.07	6.40	35.62	25.03
X.....	.....	.....	33.55	.....	.....	.....	23.30

Sample.	Soluble arsenious oxide.		Soluble arsenic oxide, extracting with 500 cc. cold water. Per cent.	Soluble calcium oxide. Per cent.
	Method 2, extrac- tion with 500 cc. cold water. Per cent.	Method 3, extrac- tion with succes- sive portions of water at 60°-70°. Per cent.		
A .....	2.43	.....	15.81	7.80
B .....	13.49	.....	7.12	6.60
C .....	3.88	.....	12.56	7.00
D .....	1.44	.....	19.56	10.80
X .....	7.88	11.90	.....	.....

FORM IN WHICH VARIOUS CONSTITUENTS APPEAR.

Knowing the full inorganic composition of the four samples given above, we are now in a position to determine the form in which they appear in London purple. The calculation is very simple. If we subtract the soluble arsenious oxide from the

<sup>1</sup> Methods 1 (precipitating with molybdate) and 2 (weighing as arsenious sulphide) were abandoned as unsatisfactory.

total arsenious oxide as such, the soluble arsenic oxide from the total arsenic oxide as such, and the soluble calcium oxide from the total calcium oxide, we have left the insoluble arsenious oxide, the insoluble arsenic oxide, and the insoluble calcium oxide. If the form in which these are united is the normal calcium arsenate,  $\text{Ca}_3(\text{AsO}_4)_2$ , and the normal calcium arsenite,  $\text{Ca}_3(\text{AsO}_3)_2$ , then the sum of the amounts of calcium oxide, necessary to unite with all the insoluble arsenious oxide to form calcium arsenite, and all of the insoluble arsenic oxide to form calcium arsenate, should be equal to the insoluble calcium oxide as determined.

We will now take up each of the samples and see if such is the case.

<i>A.</i> Total $\text{As}_2\text{O}_3 = 8.16$	Total $\text{As}_2\text{O}_5 = 33.60$	Total $\text{CaO} = 25.09$
Soluble $\text{As}_2\text{O}_3 = 2.43$	Soluble $\text{As}_2\text{O}_5 = 15.81$	Soluble $\text{CaO} = 7.80$
Insoluble $\text{As}_2\text{O}_3 = 5.73$	Insoluble $\text{As}_2\text{O}_5 = 17.79$	Insoluble $\text{CaO} = 17.29$

$$\text{As}_2\text{O}_3 : 3 \text{CaO} :: 5.73 : x$$

$$x = 4.86 = \text{CaO necessary to form } \text{Ca}_3(\text{AsO}_3)_2$$

$$\text{As}_2\text{O}_5 : 3\text{CaO} :: 17.79 : x$$

$$x = 12.99 = \text{CaO necessary to form } \text{Ca}_3(\text{AsO}_4)_2$$

$$12.99 + 4.86 = 17.85 = \text{CaO theoretically necessary to form}$$

$$\text{Ca}_3(\text{AsO}_3)_2 \text{ and } \text{Ca}_3(\text{AsO}_4)_2$$

$$17.29 = \text{CaO actually found.}$$

<i>B.</i> Total $\text{As}_2\text{O}_3 = 17.31$	Total $\text{As}_2\text{O}_5 = 26.50$	Total $\text{CaO} = 23.99$
Soluble $\text{As}_2\text{O}_3 = 13.49$	Soluble $\text{As}_2\text{O}_5 = 7.12$	Soluble $\text{CaO} = 6.60$
Insoluble $\text{As}_2\text{O}_3 = 3.82$	Insoluble $\text{As}_2\text{O}_5 = 19.38$	Insoluble $\text{CaO} = 16.99$

$$\text{As}_2\text{O}_3 : 3\text{CaO} :: 3.82 : x$$

$$x = 3.28 = \text{CaO necessary to form } \text{Ca}_3(\text{AsO}_3)_2$$

$$\text{As}_2\text{O}_5 : 3\text{CaO} :: 19.38 : x$$

$$x = 14.15 = \text{CaO necessary to form } \text{Ca}_3(\text{AsO}_4)_2$$

$$14.15 + 3.28 = 17.43 = \text{CaO theoretically necessary to form}$$

$$\text{Ca}_3(\text{AsO}_3)_2 \text{ and } \text{Ca}_3(\text{AsO}_4)_2$$

$$16.99 = \text{CaO actually found.}$$

<i>C.</i> Total $\text{As}_2\text{O}_3 = 10.47$	Total $\text{As}_2\text{O}_5 = 32.84$	Total $\text{CaO} = 24.55$
Soluble $\text{As}_2\text{O}_3 = 3.88$	Soluble $\text{As}_2\text{O}_5 = 12.56$	Soluble $\text{CaO} = 7.00$
Insoluble $\text{As}_2\text{O}_3 = 6.59$	Insoluble $\text{As}_2\text{O}_5 = 20.28$	Insoluble $\text{CaO} = 17.55$

$$\begin{aligned}
 & \text{As}_2\text{O}_3 : 3\text{CaO} :: 6.59 : x \\
 & x = 5.59 = \text{CaO necessary to form } \text{Ca}_3(\text{AsO}_3)_2 \\
 & \text{As}_2\text{O}_5 : 3\text{CaO} :: 20.28 : x \\
 & x = 14.81 = \text{CaO necessary to form } \text{Ca}_3(\text{AsO}_4)_2 \\
 & 5.59 + 14.81 = 20.40 = \text{CaO theoretically necessary to form} \\
 & \quad \text{Ca}_3(\text{AsO}_3)_2 \text{ and } \text{Ca}_3(\text{AsO}_4)_2 \\
 & 17.55 = \text{CaO actually found.}
 \end{aligned}$$

<i>D.</i> Total $\text{As}_2\text{O}_3 = 6.40$	Total $\text{As}_2\text{O}_5 = 35.62$	Total $\text{CaO} = 25.03$
Soluble $\text{As}_2\text{O}_3 = 1.44$	Soluble $\text{As}_2\text{O}_5 = 19.56$	Soluble $\text{CaO} = 10.80$
<hr/>		
Insoluble $\text{As}_2\text{O}_3 = 4.96$	Insoluble $\text{As}_2\text{O}_5 = 16.06$	Insoluble $\text{CaO} = 14.23$

$$\begin{aligned}
 & \text{As}_2\text{O}_3 : 3 \text{CaO} :: 4.96 : x \\
 & x = 4.21 = \text{CaO necessary to form } \text{Ca}_3(\text{AsO}_3)_2 \\
 & \text{As}_2\text{O}_5 : 3 \text{CaO} :: 16.06 : x \\
 & x = 11.73 = \text{CaO necessary to form } \text{Ca}_3(\text{AsO}_4)_2 \\
 & 4.21 + 11.73 = 15.94 = \text{CaO theoretically necessary to form } \text{Ca}_3 \\
 & \quad (\text{AsO}_3)_2 \text{ and } \text{Ca}_3(\text{AsO}_4)_2 \\
 & 14.23 = \text{CaO actually found.}
 \end{aligned}$$

On another sample E the results were as follows :

$$\begin{aligned}
 & 10.91 = \text{CaO theoretically necessary to form } \text{Ca}_3(\text{AsO}_3)_2 \text{ and} \\
 & \quad \text{Ca}_3(\text{AsO}_4)_2, \\
 & 10.21 = \text{CaO actually found.}
 \end{aligned}$$

It will be seen from the above calculations that the amounts of calcium oxide, arsenious oxide, and arsenic oxide are such in Samples A, B, and E as to closely approximate the formulas  $\text{Ca}_3(\text{AsO}_3)_2$  and  $\text{Ca}_3(\text{AsO}_4)_2$ . In Samples C and D the amounts of these three substances do not so closely approximate the formulas  $\text{Ca}_3(\text{AsO}_3)_2$  and  $\text{Ca}_3(\text{AsO}_4)_2$ , but show there is a tendency to form compounds in which the amount of lime is less in proportion to the arsenious and arsenic oxides as in  $\text{CaHAsO}_4$  and  $\text{Ca}_2\text{As}_2\text{O}_6$ .

I am inclined to believe from this work that the lime, arsenious and arsenic oxides in London purple are *usually* combined as the normal calcium arsenite and arsenate, but that sometimes small quantities of calcium arsenite and arsenate are formed in which the lime is less in proportion to the arsenious and arsenic oxides as in  $\text{CaHAsO}_4$  and  $\text{Ca}_2\text{As}_2\text{O}_6$ . The factors that determine this are very likely the time of boiling, the original concentration of the liquor, the presence or absence of an excess of lime and the form in which the arsenic is present in the original dye residue.

## DETECTION OF FOREIGN COLORING-MATTER IN SPIRITS.

### [SECOND METHOD.]

BY C. A. CRAMPTON AND F. D. SIMONS.

Received October 29, 1900.

A method for the detection of caramel in spirits and vinegar, based upon the selective absorption of caramel coloring-matter by fullers' earth, was published by us in this Journal.<sup>1</sup> Since that time the method has given very satisfactory results in this laboratory in the examination of samples suspected of being artificially colored, the chief difficulty encountered in its application being the variable quality and color-absorbing power of fullers' earth as found in the market. This difficulty was partially overcome by obtaining a supply of the material, of uniform color-absorbing capacity to the degree best suited to the purpose in hand, and in quantity sufficient for a very great number of tests, so that it will not be necessary to change the standards for a long time to come.

We have lately perfected, however, a much more satisfactory and convenient test, which is based simply and solely upon the insolubility in ether of the coloring-matter of caramel and prune juice, the only foreign coloring materials known by us to be used for the artificial coloring of spirits. The coloring-matter of oak wood, on the other hand (principally flavescin), is soluble in ether, which readily removes it from its solution in water or alcohol when shaken with it.

It was found that one treatment with ether was sufficient to completely remove all coloring-matter soluble therein, a second treatment with a fresh portion of ether giving no color whatever. The test is made by shaking the sample with ether, separating the ethereal from the watery layer, and comparing the color of the latter with the color of the original spirits by means of the tintometer. It is necessary, however, to bring the sample to a standard alcoholic strength, as the ether layer takes up most of the alcohol, and consequently the watery layer containing the ether-insoluble coloring-matter would be more concentrated in the case of a high proof than a low proof spirits, giving variable results. In order to insure uniformity in this respect the sample

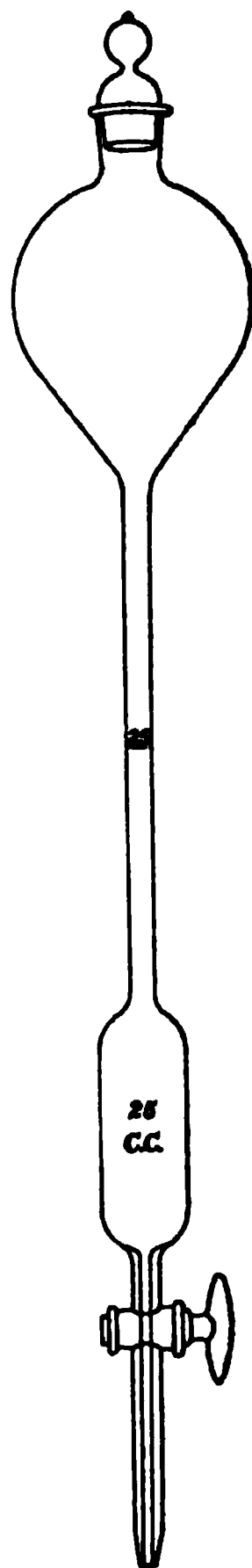
<sup>1</sup> This Journal, 21, 355 (1899).



is evaporated on the water-bath until all the alcohol has been driven off; a known quantity of water-white absolute alcohol is then added, which redissolves the coloring-matter precipitated by the removal of the alcohol, making a bright solution, which is then made up to the original volume, and its color taken by means of the tintometer. A definite portion of this solution is then treated with a definite volume of ether, the watery layer separated, and its color taken by the tintometer. A comparison of the two readings will show the character of the sample, genuine spirits giving up about 40 to 50 per cent. of its color, while spirits colored by caramel alone are entirely unaffected, the ethereal layer remaining water-white.

For making the ether extraction we have found it very convenient to use a separatory funnel, which is a slight modification or rather simplification, of Bromwell's modification of Röse's apparatus for the estimation of fusel oil in spirits.<sup>1</sup> Our apparatus is shown in the accompanying figure, and is simply an ordinary globe-shaped separatory funnel or flask with its stem above the stop-cock expanded into a bulb holding 25 cc., the graduation coming up in the stem. The upper bulb should have a capacity of about 100 cc.

Following is the detailed method of procedure: Fifty cc. of the sample under examination are measured out at a standard (room) temperature, and evaporated on the water-bath nearly to dryness; the residue is washed into a 50 cc. glass stoppered flask, 25 cc. absolute alcohol added, and the solution, after cooling to the standard temperature, is made up to the mark with water. After mixing, 25 cc. of the solution are transferred to the separatory apparatus and treated with 50 cc. ether for half an hour, being shaken at intervals; at the end of this period, the layers having separated well, the lower layer is made up with water to the original volume, 25 cc. This is conveniently accomplished by connecting



<sup>1</sup> Bull. No. 49, Chem. Div., Dept. of Agriculture, p. 115.

the lower end of the apparatus with a rubber siphoning tube which carries water from an elevated flask, the inflow of water being regulated by the stop-cock of the apparatus. The contents of the flask are again shaken, and again allowed to separate (whereby the volume of the lower layer is slightly increased), and the watery layer is drawn off through the stop-cock for a reading of its color in the tintometer. At the same time a reading is taken of the 25 cc. of the solution which was not subjected to the treatment with ether; from these two readings the amount of color extracted by ether is calculated in percentages.

The accuracy of the test is much promoted by adhering carefully to the same conditions throughout, especially with regard to temperature.

Applied to a series of 34 samples of spirits known to be naturally colored, the test gave the following results:

	Color removed. Per cent.
Maximum.....	51.1
Minimum.....	36.4
Average.....	41.7

A series of 17 samples known to be artificially colored gave the following figures:

	Color removed. Per cent.
Maximum.....	23.2
Minimum.....	0.0
Average.....	14.8

The results do not show quite so wide a variation between the two sets of samples as the results obtained from the same samples by the fullers' earth test, but the ether extraction method is more satisfactory in a general way. The results obtained by the two methods were confirmatory in every case, and the former will be valuable as a supplementary test. In comparing the figures it must be kept in mind that the results by the two methods are in opposite directions; that is, fullers' earth removes the color from an artificial spirit, while ether removes the color from a natural spirit.

Since the work on this test was completed our attention was drawn to an article by Leach,<sup>1</sup> wherein he recommends the

<sup>1</sup> This Journal, 22, 207 (1900).

detection of caramel coloring in milk by means of its insolubility in ether, or rather its separation in this way from other coloring-matters (annatto and aniline orange), its identification by "any of the usual tests" to follow.

We have found the method inapplicable to vinegars colored with caramel, genuine apple vinegar giving no color when shaken with ether.

LABORATORY OFFICE OF INTERNAL REVENUE,  
U. S. TREASURY DEPARTMENT, WASHINGTON, D. C.

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[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION  
OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

## A RAPID METHOD FOR THE DETECTION OF "ANILINE ORANGE" IN MILK.

BY HERMANN C. LYTHGOE.

Received October 31, 1900.

**D**URING the year ending September 30, 1900, there have been examined by the Department of Food and Drug Inspection of the Massachusetts State Board of Health 6137 samples of milk, of which number 45, or 0.7 per cent., contained foreign coloring-matter. Of these colored samples, 20 contained annatto, 3 contained caramel and 22, or 48 per cent., contained "aniline orange" which generic term is used to describe those azo colors used for this purpose. The statistics of the previous five years show that 0.6 per cent. of the total samples of milk were artificially colored, of which 10 per cent. contained aniline orange. The statistics of 1900 show a decided increase in the use of aniline orange as a milk "improver."

In view of the facts that if a sample is carefully colored with a view of not getting in too much, that many samples containing color are above the legal standard and that it is very difficult to tell at a casual glance whether or not a sample is colored, a rapid method for the detection of foreign coloring-matter in milk would be invaluable to the milk analyst.

In testing a sample of milk for formic aldehyde by the well-known method of boiling with an equal volume of strong hydrochloric acid containing ferric chloride,<sup>1</sup> the writer found upon

<sup>1</sup> See Twenty-ninth Annual Report of the Massachusetts State Board of Health, 1897, p. 558.

mixing the cold acid with the milk that the resulting curd was of an intense pink color. Upon further examination by the method of A. E. Leach<sup>1</sup> the sample was found to contain aniline orange. As a result of this, the following method is offered for the detection of aniline orange in milk.

Place about 15 cc. of milk in a porcelain casserole and add about the same quantity of hydrochloric acid (sp. gr. 1.20) gently shaking the casserole to cause thorough mixing and to break up the curd into rather coarse lumps. If the milk contains aniline orange the curd will be colored pink while if it be free from the color, the curd will be white or yellowish, according to the natural color of the milk.

If it is desired to test the milk for formic aldehyde, this same solution may be boiled after the usual addition of a drop of ferric chloride solution and if it be present the usual purple color will appear. The presence of both substances has no effect upon either test.

Commercial hydrochloric acid to which ferric chloride has been added may be used provided that the solution is not too yellow. It has been the custom in this department to add 5 cc. of a 10 per cent. solution of ferric chloride to 2 liters of commercial hydrochloric acid, and to use this solution in testing for aniline orange and formic aldehyde in milk. Sulphuric acid cannot be employed for this purpose.

This test has been in use in this department during the past year and has given satisfactory results.

It is unfortunate that this test does not detect annatto and caramel for the analyst frequently labors in vain upon suspicious looking samples, but by applying this simple method, all the samples colored with aniline orange will be pointed out at the same time that the analyst makes the test for formic aldehyde, without the loss of time, reagent, or sample.

<sup>1</sup> A. E. Leach : This Journal, 20, 207 (1900).

## NOTE.

*Preparation of Triphenylchlormethane.*—In my paper on “The Preparation of Triphenylchlormethane,” in the November number, page 752, this Journal, a misstatement occurs which gives an ambiguous meaning to the paper. The first paragraph should read : “It is generally stated \* \* \* *triphenylmethane* is the principal product of the reaction,” and not *triphenylchlormethane*, as it reads now.

I also wish to take this opportunity to state that Thorp (“Inorganic Chemical Preparations,” p. 39) recommends the preparation of aluminum chloride, in small quantities, by the same method as given in my paper.

M. GOMBERG.

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## NEW BOOKS.

**DIE ÄTHERISCHEN ÖLE.** Von E. GILDEMEISTER und FR. HOFFMANN, bearbeiten im auftrage der firma Schimmel & Co. in Leipzig. Berlin: verlag von Julius Springer. 1899.

**THE VOLATILE OILS.** By E. GILDEMEISTER and FR. HOFFMANN. Written under the auspices of the firm of Schimmel & Co., Leipzig. Authorized translation by EDWARD KREMERS, Madison, Wis. Milwaukee: Pharmaceutical Review Publishing Co. 1900.

**THE CHEMISTRY OF ESSENTIAL OILS AND ARTIFICIAL PERFUMES.** By ERNEST J. PARRY, B.Sc., etc. London: Scott, Greenwood & Co. 1899. New York: D. Van Nostrand Company.

The subject of the essential or volatile oils has until very recently been given a distinctly secondary place in the chemical text-books in comparison with the class of fixed oils. Indeed, a few lines about terpenes and camphors has been thought quite a sufficient treatment by the writers of some of the most reputable text-books until quite lately. But this state of things could not remain in view of the brilliant work done in recent years in this branch by men like Wallach, Tiemann, and von Baeyer. As Prof. Emil Fischer, of Berlin, has recently remarked, it is a chapter of organic chemistry that has undergone more rapid development within the past fifteen years than any other.

It is fortunate that, the need having been felt, it should have been filled by the firm of Schimmel & Co., of Leipzig, who are so intimately and honorably connected with the industry of the

essential oils, stepping forward and commissioning scholarly and competent men like Drs. Gildemeister and Hoffmann to write a book covering this ground. The result is the magnificent volume before us in which, as Prof. Kremers says, we find a happy blending of history with chemical science and technology that is quite unique in modern chemical literature.

With true German thoroughness, the work begins with an Historical Introduction, in which we have an account of the spice trade in antiquity and during the middle ages, illustrated by two colored charts, showing "the highways of commerce" in ancient times and in the middle ages, respectively.

This introduction also contains a history of volatile oils, and a history of the methods of distillation and of distilling apparatus. This portion of the work shows much antiquarian knowledge and research and is from the pen of Dr. Fr. Hoffmann, the former editor of the "Pharmaceutische Rundschau," of New York, now resident in Berlin. It is copiously provided with bibliographic references and is of very great interest to the historical student.

The General Part which follows, discusses first the theoretical basis for obtaining volatile oils by steam distillation and then takes up for enumeration and scientific description the more commonly occurring constituents of volatile oils. This descriptive part is very valuable to the chemist, as it epitomizes the latest and most accurate results in this group, and gives full references to the journal literature in foot-notes. This is followed by an account of the methods of examination of volatile oils, both physical and chemical, and lastly we have a list of plants arranged according to families, from which volatile oils are obtained.

The third and longest division of the book is the Special Part, in which we have the history, origin, preparation, properties, composition, examination, and commercial statistics of the volatile oils. The number of individual oils so treated in detail in the original German work is 422, and in Prof. Kremers' translation 430.

Besides the two colored charts already referred to as found in the Historical Introduction, we have two colored maps of Ceylon and of Calabria and Sicily, respectively, and numerous wood-

cuts illustrating the conditions of production of some of the essential oils.

The German publication forms a stately volume of 919 pages, bound in half morocco, and will form a most satisfactory addition to any chemical library.

A few words specially with regard to the American edition. In Prof. Kremers, of the University of Wisconsin, the authors found a most competent translator and editor for the English issue, as it is a field in which he has himself made valuable contributions and with which he is entirely familiar. By condensing several of the sections in the Historical Introduction and putting the bibliographical notes together at the end of the book he has been able to bring all the matter in the compass of 733 pages, without sacrifice of any important feature.

The charts and illustrations are all reproduced and the book is well printed and finely bound.

The work of Mr. Parry on "The Chemistry of Essential Oils and Artificial Perfumes," which also appeared in 1899, while not so ambitious a work as that of Drs. Gildemeister and Hoffmann is, nevertheless, a valuable work, written throughout in a scientific spirit and with a careful consideration of available sources of information. Without attempting anything in the way of a history of the subject, it starts in with the general properties of the essential oils briefly stated, and then gives an excellent review of the compounds occurring in essential oils, stating the most approved views with the aid of structural formulas. The sections on the preparation and analysis of the essential oils are relatively brief and deal with the subject only in a general way. The systematic study of the oils, which takes up the body of the book, deals with them according to the botanical relationship of the plants yielding them, that is, according to natural orders. This part seems to have been well done and the journal literature is considered throughout. A chapter on terpeneless oils follows. The chemistry of artificial perfumes, to which 41 pages are devoted, is well treated, in fact is the best summary of our knowledge which, as far as the writer knows, has appeared in the English language. It makes frequent reference to the patent literature, giving numbers and dates of patents, giving an account of the ionone and violet-oil patent litigation, quoting Tiemann's

and Fritsche & Co.'s patents in full, explains the methods for the manufacture of vanillin, heliotropin, artificial musk, hyacinth, etc. The appendix contains a valuable table of the constants for the more important essential oils. The book can be thoroughly commended as furnishing a compact and convenient reference book on the subject. **SAMUEL P. SADTLER.**

**CHEMISCH-TECHNISCHE UNTERSUCHUNGSMETHODEN.** Herausgegeben von **DR. GEORG LUNGE.** Dritter Band, mit 104 abbildungen. Vierte auf-  
lage. xxii + 1082 pp. Berlin: Verlag von Julius Springer. 1900.  
Price, M. 23.

This volume contains Mineral Oils and Examination of Lubricants, by Dr. D. Holde; Oils and Fats and Special Methods of the Oil and Fat Industry, by Dr. Rob. Henriques; Examination of Resins, Balsams and Gum Resins, and Drugs and Galenical Preparations, by Dr. Karl Dieterich; Caoutchouc and Caoutchouc Wares, by Dr. Rob. Henriques; Ethereal Oils, by Dr. E. Gildemeister; Raw Materials, Products, and By-products of Sugar Manufacture, by Dr. O. von Lippmann and Dr. Georg Pulvermacher; Starch, by Dr. C. von Eckenbrecher; Spirits, by Dr. A. Ebertz; Brandy and Liqueurs and Vinegar, by Dr. G. Schüle; Examination of Wine, by Dr. Karl Windisch; Beer, by Prof. L. Aubry; Examination of Vegetable Material Containing Tannin, by Dr. C. Councler; Leather, by Dr. Joh. Paessler; Paper, by W. Herzberg; Ink, by O. Schluttig and Dr. G. S. Newmann; Organic Preparations, by Dr. J. Messner; The Tartaric Acid Industry and Citric Acid Manufacture, by Dr. Hermann Rasch; and Organic Dyes and the Examination of Textile Fibers and Loading Materials, by Dr. R. Gnehm.

This is a wide range of subjects, which seem in the main to be well covered. The authors confine themselves very closely to methods of testing. Very little is said about methods of manufacture. This seems on the whole something of a defect, for while it is true that information of this sort is otherwise attainable, it is widely scattered and one of the chief values of such a compilation as this is found in the saving of the time of the busy working chemist. Very few chemists can expect to fully cover, even in analytical knowledge, so wide a range as is here presented.

The "Anhang" contains numerous tables from the body of the work printed on one side of the paper for pasting on the



laboratory wall. Some of these tables are: Correction of the Specific Gravity of Petroleum for Different Temperatures; Specific Gravity of Aqueous Glycerine Solutions; Refractive Index of Aqueous Glycerine Solutions; Specific Gravity of Methyl Alcohol; Specific Gravity of Mixtures of Ortho- and Paratoluidin; Determination of Monoethyl and Diethyl Anilin; Solidifying Points of Acetic Acid; Specific Gravity of Oxalic Acid Solutions.

The book is a monument of patient industry and is worth more than it costs. It is a good piece of book work mechanically considered.

E. H.

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Bulletin of the United States Geological Survey, No. 176. Some Principles and Methods of Rock Analysis. 114 pp.

The Hessian Fly in West Virginia and How to Prevent Losses from its Ravages. By A. D. Hopkins, Ph.D. Bulletin 67. W. Va. Agricultural Experiment Station, Morgantown, W. Va. August, 1900. 16 pp.

Report on the Geology of the Essequibo, Potaro, Konawaruk and Demerara Rivers, British Guiana. Georgetown, Demerara. 1900. 82 pp. 4to.

Quantitative Chemical Analysis, adapted for use in the Laboratories of Colleges and Schools. By Frank Clowes, D.Sc. (Lond.), and J. Bernard Coleman, A. R. C. Sc. (Dublin). Fifth Edition. Philadelphia: P. Blakiston's Son & Co. 1900. xxiv + 592 pp. Price \$3.50.

Decision of the U. S. Circuit Court of Appeals on the Indoine Blue Case. 27 pp. Kuttroff, Pickhardt & Co., P. O. Box 2885, New York City.

Chemisch-technische Untersuchungsmethoden. Herausgegeben von Dr. Georg Lunge. Dritter Band, mit 104 in den Text gedruckten Abbildungen. Vierte vollständig umgearbeitete und vermehrte Auflage. Berlin: Verlag von Julius Springer. 1900. xxii + 1082 pp. Anhang iv + 55. Price, 23 marks.

Victor Von Richter's Textbook of Inorganic Chemistry, edited by Prof. H. Klinger, University of Königsberg. Authorized Translation by Edgar F. Smith, Professor of Chemistry in the University of Pennsylvania. Assisted by Walter T. Taggart, Instructor in Chemistry. Fifth American from the Tenth German Edition, carefully revised and corrected. With 68 illustrations in wood and colored lithographic plate of spectra. Philadelphia: P. Blakiston's Son & Co. 1900. xii + 430 pp. Price, \$1.75.

An Investigation into the Causes of So-called Uric-acid Lesions,

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A Handbook of Industrial Organic Chemistry Adapted for the Use of Manufacturers, Chemists, and all Interested in the Utilization of Organic Materials in the Industrial Arts. By Samuel P. Sadtler, Ph.D., F.C.S. Third Revised and Enlarged Edition. Philadelphia: J. B. Lippincott & Co. 1900. Price, \$5.00.

Chemical Technology or Chemistry in its Applications to Arts and Manufactures. Edited by Charles Edward Groves, F.R.S., and William Thorp, B.Sc., with which is Incorporated Richardson and Watts' Chemical Technology. Vol. III.—Gas Lighting. By Charles Hunt. Illustrated. Philadelphia: P. Blakiston's Son & Co. 1900. Price, \$3.50.

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PROCEEDINGS

OF THE

AMERICAN CHEMICAL SOCIETY

---

FOR THE YEAR 1900.

EASTON, PA.:  
THE CHEMICAL PUBLISHING COMPANY.  
1900.



# PROCEEDINGS.

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Issued with January Number, 1900.

## Proceedings.

### COUNCIL.

#### NAMES PROPOSED FOR MEMBERSHIP.

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Ballard, J. Clarence, U. S. Exp. Station, Lafayette, Ind.  
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Cohoe, Wallace P., 14 Boylston Hall, Cambridge, Mass.  
Colhane, Daniel F., 58 Moore St., Cambridge, Mass.  
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Davis, Robert S., 1330 12th Ave., Altoona, Pa.  
Downey, James E., 10 Taylor St., Holyoke, Mass.  
Earle, Richard B., 403 Craigie Hall, Cambridge, Mass.  
Gardunio, Jesur, Aguascalientes, Mexico.  
Hale, William Jay, 42 Kirkland St., Cambridge, Mass.  
Havens, Franke S., 9-13 Mercer St., New York, N. Y.  
Jandrier, Edmond, Peace Dale, R. I.  
Jerome, Alexander, 502 W. 45th St., New York City.  
Kittredge, Harvey G., Dayton, Ohio.  
Krebs, H. J., Wilmington, Del.  
MacIntosh, Douglas, 208 E. 61st St., N. Y. City.  
Sandford, William E., Kewanee, Ill.  
Sanger, Charles R., Walker St., Cambridge, Mass.  
Schaak, Milton F., 108 Penn St., Brooklyn, N. Y.  
Williams, Simon E., Boylston Hall, Cambridge, Mass.

#### NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Craig, Archibald G., 5516 Graham Pl., Pittsburg, Pa.  
Gearing, James H., 2111 Sidney St., Pittsburg, Pa.  
Stifel, Walter H., 1319 Locust St., Allegheny, Pa.  
Waters, Oliver G., 223 5th Ave., Pittsburg, Pa.  
Wells, Allan, 213 South St. Clair St., Pittsburg, Pa.

## MEMBERS ELECTED DECEMBER 30, 1899.

Adams, Walter Owen, 1776 Massachusetts Ave., No. Cambridge, Mass.

Ayer, Harold, Mass. Inst. Tech., Boston, Mass.

Baldwin, Charles E., 197 Auburn St., Cambridge, Mass.

Barnes, Bayard, Yale Univ., New Haven, Conn.

Beans, Hal T., Univ. of Nebr., Lincoln, Nebr.

Boggs, Gilbert H., 603 S. 42nd St., Philadelphia.

Boltwood, Bertram B., Sheffield Scientific School, New Haven, Conn.

Breer, Louis B., Builders Iron Foundry, Providence, R. I.

Button, Ok, Box 233, Trenton, Mich.

Chase, March F., Mineral Point Zinc Co., Mineral Point, Wis.

Cluff, C. B., Lowell Textile School, Lowell, Mass.

Croftan, Alfred C., Vandevort Block, Pasadena, Cal.

Cross, Walter Martin, 12th and Troost Sts., Kansas City, Mo.

Denham, Henry H., 146 N. Pearl St., Buffalo, N. Y.

Doolittle, R. E., Mich. State Dairy and Food Com., Lansing, Mich.

Dustin, Guy K., 51 Prospect St., New Haven, Conn.

Gerlach, Oscar, Mich. Cement Co., Coldwater, Mich.

Green, Erik H., 112 Newbury St., Boston, Mass.

Grosse, S. P., 180 6th Ave., Brooklyn, N. Y.

Hamilton, Louis P., 3417 Hamilton St., Philadelphia.

Hopkins, Arthur J., Amherst, Mass.

Jackson, Florence, Wellesley College, Wellesley, Mass.

Johnson, Treat B., 141 College St., New Haven, Conn.

Knapp, Rudolf E., Parke, Davis & Co., Detroit, Mich.

Lichtenstein, Alfred F., 134 Amity St., Brooklyn, N. Y.

Locke, James, Sheffield Chem. Lab., New Haven, Conn.

Loew, Oscar, Dept. of Agr., Washington, D. C.

Manteuffel, Adolf, Somerset Chem. Co., Bound Brook, N. J.

McFarland, B. W., 278 Canner St., New Haven, Conn.

Meyer, Gustave M., 59 E. 77th St., New York City.

Mixter, Wm. E., New Haven, Conn.

Moore, F. J., Mass. Inst. Tech., Boston, Mass.

Munson, L. S., Dept. of Agr., Washington, D. C.

Newton, Elmer S., 3018 Cambridge Pl., Washington, D. C.

Norman, George M., Ill. Steel Co., South Works, Chicago.

Parker, C. Leroy, Patent Office, Washington, D. C.

Peet, B. W., Ypsilanti, Mich.

Pemberton, Ralph, 1947 Locust St., Philadelphia.

Phalen, Wm. C., School of Mines, Socorro, N. M.

Phelps, Isaac King, Kent Chem. Lab., New Haven, Conn.

Platt, Elbert S., Waterford, N. Y.

Post, Frank I., 243 E. 76th St., Chicago.

(3)

Schoonmaker, Harry, 124 S. Main St., Los Angeles, Cal.  
Skinner, Hervey J., 15 Chestnut St., Wakefield, Mass.  
Stead, John E., 11 Queen's Terrace, Middlesbrough, England.  
Sullivan, Eugene C., 331 Packard St., Ann Arbor, Mich.  
Tucker, Charles W., 8 Grover St., Lynn, Mass.  
Voorhees, Gerald E., Berwick, Pa.  
Wachter, Leonard M., 45 James St., Green Island, N. Y.  
Wheeler, Henry L., Sheffield Chem. Lab., New Haven, Conn.  
Worstall, Robert A., Purdue Univ., Lafayette, Ind.

ASSOCIATES ELECTED DECEMBER 30, 1899.

Boroschek, Leopold, 149 E. 56th St., N. Y. City.  
Clark, Edwin H., 17 Hillhouse Ave., New Haven, Conn.  
Gillet, Ransom H., Pafraets Dael Club, Troy, N. Y.  
Goodenough, Robert J., 18 7th Ave., Brooklyn, N. Y.  
McCrudden, Francis H., 134 Castle St., Boston, Mass.  
Merriam, Henry F., Summit, N. J.  
Mihalovitch, Sidney F., 829 Hutchins Ave., Avondale, Cincinnati, O.  
Olshausen, Bruno, Stanford Univ., Cal.  
Rising, Herbert Robinson, 101 Wall St., New Haven, Conn.  
Shilstone, Herbert M., 114 Pearl St., N. Y. City.  
Sullivan, Robert Barry, 111 Grove St., New Haven, Conn.  
Swenarten, W. Hastings, 169 Union St., Montclair, N. J.  
Victor, Carl Louis, 101 Wall St., New Haven, Conn.  
Webb, Ernest H., 1256 Massachusetts Ave., Cambridge, Mass.

CHANGES OF ADDRESS.

Blair, A. W., Expt. Sta., Lake City, Fla.  
Cushman, Allerton S., Bryn Mawr College, Bryn Mawr, Pa.  
Davis, W. W., care Va. Iron, Coal, and Coke Co., Bristol, Tenn.  
Goldstein, Harris, 228 Henry St., N. Y. City.  
James, J. H., Sault Ste. Marie, Ont.  
Lorenz, H. W., Box 4028, Philadelphia, Pa.  
Smith, E. A., Republic, Wash.  
Wesson, David, care Southern Cotton Oil Co., Savannah, Ga.

ADDRESS WANTED.

Schoen, Joseph, formerly of 3602 Lake Ave., Chicago, Ill.  
Wood, J. R., formerly of 439-441 Green St., Philadelphia, Pa.

## MEETINGS OF THE SECTIONS.

## WASHINGTON SECTION.

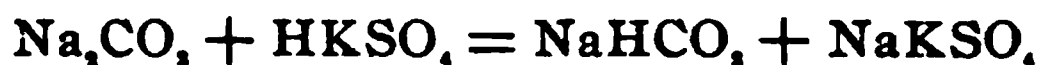
The regular meeting was held October 12, 1899.

The first paper was read by Mr. J. K. Haywood and was entitled "The Determination of Glycogen," by J. K. Haywood and W. D. Bigelow.

The authors proved that methods for the estimation of glycogen, which depend on its direct inversion into dextrose, are unreliable and have modified the method of Brücke so as to make it accurate and fairly rapid.

The second paper was read by Dr. F. K. Cameron and was entitled "A Method for Estimating Black Alkali in Soils."

The method enables the determination of the degree of hydrolyzation of the sodium carbonate in soils and soil crusts containing this compound. It was shown that an accurate determination of the amount of sodium carbonate could not be made by titrating directly with a standard acid, two reactions taking place with the formation of the acid carbonate in varying quantities and furthermore the probable existence of acid carbonate in the soil adds to the difficulty of such a determination. It was shown that acid potassium sulphate is free from these objections, the reaction taking place with quantitative exactness according to this equation :



both substances indicated in the right-hand member of the equation being natural. It should be borne in mind that acid sodium carbonate although a neutral substance towards indicators, quite rapidly and readily inverts with the formation of the alkaline normal carbonate, so that a reasonable degree of speed must be used in making the titrations.

Details of the practical application of the method with examples from practice, were given, and it was shown that in ordinary practice the method was easily capable of an accuracy indicated by a probable error of less than 0.02 per cent.

The last paper was read by Dr. H. W. Wiley, and was entitled "The Fifteenth Annual Meeting of the Association of Official Agricultural Chemists, at San Francisco, July 5-7, 1899."

Mr. Tassin exhibited a specimen of calcium chloride which he



had obtained from a muck soil found in Utah. The salt occurs as an incrustation between Salt Lake City and Salt Lake.

Dr. Bolton exhibited a bibliography of thallium compiled by Miss Martha Dunn and recently published by the Smithsonian Institute. He called attention to the work done in Paris by Jules Garcon, who has published a bibliography of the "Chemical Technology of Textile Fibers," and a pamphlet entitled "Resources of Bibliography of Chemistry." The latter consists of a list of chemical bibliographies.

The regular meeting was held on November 9, 1899.

The first paper of the evening was read by Dr. H. Carrington Bolton and was entitled "Reminiscences of Bunsen and the Heidelberg Laboratory, 1863-65."

The speaker related anecdotes of Bunsen, and events that occurred in the Heidelberg Laboratory during the third semester which he spent there. Contemporary with him were the following Americans :

Eli W. Blake, afterwards professor of physics, Brown University, deceased ; Owen W. Root, afterwards professor of chemistry, at Hamilton College, N. Y., deceased ; Charles Wolf, of Cincinnati, deceased ; Frank Slingluff, of Baltimore ; Harry McBurney, of Boston ; Lyman Nichols, of Boston ; Arnold Hague, of the U. S. Geological Survey.

The second paper of the evening was read by Dr. H. Carrington Bolton and was entitled "Chapters on the History of the Thermometer ; I.—The Open Air Thermoscope of Galileo."

The primitive form of the thermometer was invented about the year 1595 by Galileo ; this is proved by extant letters addressed to him by his pupil and friend Sagredo. The instrument was an open air thermoscope of the inverted type, and was early applied to meteorological observations, to testing the temperature of fever patients, and to noting temperature of freezing-mixtures.

The very common statement that the thermometer was the invention of C. Drebbel, of Holland, has no basis of fact, as shown by his own publications, copies of which were exhibited by the speaker.

The third paper was read by Dr. F. W. Clarke and was entitled "The Action of Ammonium Chloride upon Certain Silicates," by F. W. Clarke and George Steiger.

The authors described a series of experiments in which various silicates were heated in a sealed tube to 350° C. with dry ammonium chloride. After leaching out the contents of the tube with water it was found that alkalies were removed as chlorides and replaced by ammonia. Analcite and leucite are thus transformed into an ammonium leucite :



which is perfectly stable at 300° and only begins to decompose when heated in the open air to 350°.

Some eight other silicates were given preliminary study and the reaction was found to be fairly general. The product from natrolite contained 8.3 per cent. of ammonia and other zeolites took up from 4 to 6 per cent. The investigations are to be continued.

The fourth paper was read by Dr. F. K. Cameron and was entitled "Hydrochloric Acid and Aqueous Phenol," by F. K. Cameron and J. A. Emory.

The authors determined the freezing-point curve for hydrochloric acid solutions, saturated with respect to phenol. Each independently determined the concentrations of the various solutions and their freezing-points for intercomparison. The curve was found to be a straight line, parallel to the curve for water and hydrochloric acid alone, from which it would seem that the solubility of phenol is practically constant through the range of temperature involved, and the lowering of the freezing-point of the solvent is a purely additive effect of the two solutes.

The fifth paper was read by Dr. F. K. Cameron and was entitled "The System Water, Hydrochloric Acid, and Phenol," by F. K. Cameron and W. H. Krug.

On lowering the temperature of the system, solid phenol separates. But if the initial mass of water be relatively large its concentration with respect to hydrochloric acid is practically unaffected while the solid phenol is separating and consequently the temperature of the phenol remains very constant. The freezing-point curve for phenol in contact with aqueous solutions of

hydrochloric acid of various concentrations, was determined. Its practical value for a rapid determination of the approximate strength of hydrochloric acid solutions was indicated.

WILLIAM H. KRUG, *Secretary*.

#### CHICAGO SECTION.

The November meeting of the Chicago Section was held at the Technical Club, November 24, 1899.

After the usual dinner, Prof. Julius Stieglitz, of the University of Chicago, gave a very interesting paper on the "Theory of Ionization in Analytical Chemistry."

He showed the value of the theory in explaining analytical reactions, thus adding to the scientific side of purely analytical chemistry. His remarks were illustrated with many experiments.

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The thirty-first meeting of the Chicago Section was held at the Technical Club, December 13, 1899.

The following program was presented :

"An Apparatus for the Distillation of Ammonia with Steam," by Edward Gudeman.

"Notes on the Determination of Arsenic in Antimonial Lead," by Gustav Thurnauer.

"On the Action of Acyl Chlorides on the Disubstituted Ureas," by F. B. Dains.

These officers were elected for the year 1900: *President*, W. R. Smith; *Vice-President*, Geo. H. Ellis; *Treasurer*, C. W. Patterson; *Secretary*, F. B. Dains; *Executive Committee*, The President, the Secretary, Wm. Hoskins; *Member of the Council*, E. Gudeman.

F. B. DAINS, *Secretary*.

#### NORTH EASTERN SECTION.

The regular monthly meeting of the section was held in Boston on Wednesday evening, November 22. President A. D. Little called the meeting to order, 68 members being present. After the secretary's minutes were read and approved, the election of three members to represent the section in the council was held. The members elected were H. P. Talbot, L. P. Kinnicut, and T. W. Richards.

Fred. L. Dunlap, of Worcester, presented a paper on "Cata-

lytic Action, with Special Reference to Its Application to the Manufacture of Sulphuric Acid." The second paper was by Walter L. Jennings, of Worcester, on "The Constitution of Rosaniline Dye Stuffs." At 10.30 the meeting adjourned.

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The December meeting of the section was held in Boston on December 16, President Little in the chair, and 52 members present. After transacting the regular business of the section, Mr. A. D. Little presented a paper on "Viscose (cellulose sulphocarbonate) and Its Applications."

Mr. Little gave a review of the chemistry of cellulose, explained the method of preparation of viscose, and described some of its many applications, illustrating the paper by experiments and samples. After a discussion of the paper the section adjourned.

W. H. WALKER, *Secretary.*

100

*Edward W. Mosley.*

Issued with February Number, 1900.

## Proceedings.

### MINUTES OF THE TWENTIETH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The meeting was called to order at 9.15 A.M., Wednesday, December 27, 1899, in the Kent Chemical Laboratory, Yale University, New Haven, Conn., with President Edward W. Morley in the chair. Professor S. W. Johnson, of Yale University, was introduced and in a brief address extended a cordial welcome to the visiting chemists. President Morley responded in behalf of the Society.

The minutes of the previous meeting were approved as recorded in the secretary's book.

Papers were then read and discussed as follows: "The Action of Ammonium Chloride upon Certain Silicates," by F. W. Clarke and George Steiger; read by Professor Clarke. The paper was discussed by Messrs. Johnson and Clarke.

"The Specific Gravity of Copperas Solutions Containing Free Sulphuric Acid," by Edward Hart.

"The Allotropic Forms of Selenium," by A. P. Saunders. Discussed by Messrs. Dennis and Saunders.

"Synthesis of 2-3,3-Trimethylcyclopentanone," by W. A. Noyes; read by Edgar F. Smith.

"The Action of Unsymmetrical Phenyl-hydrazines on Chlorquinones," by Wm. McPherson; discussed by Messrs. Bogert, McPherson, and Freer.

A motion to appoint a representative from the American Chemical Society to act together with representatives from other organizations, in case it should be found desirable, to constitute a committee to consider the claims of chemistry in courses of education was, upon motion of Professor Atwater, referred to the council with power.

A paper by L. P. Kinnicutt and George R. Sanford on "The Iodometric Determination of Small Quantities of Carbon Monoxide," was read by Dr. Kinnicutt.

W. O. Atwater then presented a paper on "The Conservation of Energy in the Living Organism," and in connection with the paper explained the respiration calorimeter used in investigations upon the subject at Wesleyan University, Middletown, Conn.

After some announcements the morning session was adjourned.

WEDNESDAY AFTERNOON, DECEMBER 27, 1899.

A visit was made to Middletown, under the leadership of Professor W. O. Atwater, for the purpose of inspecting the laboratories and buildings of Wesleyan University, and witnessing the method of conducting investigations with the respiration calorimeter.

Before returning to New Haven, the visiting chemists enjoyed the hospitality of Professor Atwater and his family at his home where light refreshments were served.

WEDNESDAY EVENING, DECEMBER 27, 1899.

The address of the retiring president, Edward W. Morley, was delivered in Osborn Hall, at 8 P.M.: Subject, "Are New Processes Needed for the Determination of the Atomic Weight of Oxygen?"

After the president's address the chemists enjoyed a "smoker" at the New Tontine Hotel where Professor Wm. H. Brewer entertained them with some reminiscences of old chemists.

THURSDAY MORNING, DECEMBER 28, 1899.

The session was called to order in the Sheffield Chemical Laboratory, at 9.15 A.M. The reports of the secretary and the editor were read and ordered placed on file, as was also the report of the Committee on Papers and Publications.

The reports of the acting librarian and of the Finance Committee were read and referred to the Council. F. W. Clarke then presented the report of the Standing Committee on Atomic Weights and the report of the International Committee on Atomic Weights. The former was referred to the Committee on Papers and Publications and, on motion of Dr. McMurtrie, the report of the International Committee on Atomic Weights



was adopted, the president was authorized to appoint the necessary committee, and the other officers were empowered to carry out the recommendations of the report.

The report of the treasurer was read and placed on file.

A communication was received from E. E. Ewell, chairman of the Committee on Standards for Instruments of Measure, in which certain resolutions were presented to the Society. On motion of Dr. Talbot the communication and resolutions were referred to the Committee on Standards for Instruments of Measure for consideration and report to the council of the Society, which was requested to take action in the matter, and the Committee on Standards for Instruments of Measure was empowered to increase its number for the purpose of considering this subject.

Dr. McMurtrie made an announcement regarding the Fourth International Congress of Applied Chemistry which is to be held in Paris during the coming summer.

The results of the balloting, in the annual election for councilors and president, were announced by President Morley as follows: Councilors at large, elected to serve for three years, beginning January 1, 1900, F. W. Clarke, F. P. Venable, Chas. F. Mabery, and S. P. Sadtler; President of the Society for the year 1900, Wm. McMurtrie. Dr. McMurtrie, the president-elect, was then introduced by President Morley and made a few remarks in appreciation of the honor conferred upon him.

The following papers were presented: "A Demonstration of the Properties of the Isomeric Form of Potassium Ferricyanide," by James Locke; "Bacterial Treatment of Sewage in England," by L. P. Kinnicutt; "Preparation of Samples for Analysis," by S. W. Johnson; "What is Plant Food?" by H. W. Wiley.

The report of the Committee on Patent and Related Legislation was received and placed on file.

On motion of H. W. Wiley, the thanks of the Society were extended to:

The faculty and corporation of Yale University, the officers in charge of the Connecticut Agricultural Experiment Station, the Local Committee of Arrangements for the Meeting, Professor Wm. H. Brewer, Professor W. O. Atwater, the New Haven Colony Historical Society, the governors of the Graduates' Club,

the citizens of New Haven, and the trustees of the Chemists' Club of New York, for hospitalities and courtesies shown to the visiting chemists and for their untiring and successful efforts to make the Twentieth General Meeting of the American Chemical Society a most enjoyable and memorable occasion.

The Society then adjourned to meet at the New Tontine Hotel at 7 P.M.

THURSDAY AFTERNOON, DECEMBER 28, 1899.

The council met in the Kent Chemical Laboratory at 2 P.M.

The afternoon was spent by the other members of the Society in visiting the buildings, laboratories, and collections of Yale University, etc.

THURSDAY EVENING, DECEMBER 28, 1899.

The members of the Society enjoyed a subscription dinner at the New Tontine Hotel. The retiring president, Edward W. Morley, presided and H. W. Wiley acted as toast-master.

Toasts were responded to as follows :

"The Retiring President"—Edward W. Morley. "The Incoming President"—Wm. McMurtrie. "Agricultural Chemists"—S. W. Johnson. "Old Bachelorhood"—Chas. B. Dudley. "Lady Members of the Society"—Charlotte A. Bragg. "The New York Section"—Chas. F. McKenna. "The Rhode Island Section"—E. D. Pearce. "The Northeastern Section"—L. P. Kinnicutt. "The Washington Section"—H. N. Stokes. "The Philadelphia Section"—Edgar F. Smith. "The Michigan Section"—Paul C. Freer. "The Lehigh Valley Section"—Edward Hart. "The Local Committee"—H. L. Wells.

The Twentieth General Meeting of the American Chemical Society then adjourned *sine die*.

ALBERT C. HALB, *Secretary*.

ANNUAL REPORT OF THE SECRETARY OF THE AMERICAN  
CHEMICAL SOCIETY, DECEMBER 26, 1899.

The past year of the Society has been one of continued progress and development. The membership has increased from 1415 to 1569; two new sections have been formed, one in Philadelphia, the other in Michigan with headquarters at Ann Arbor; a fund has been permanently invested to cover all

amounts that have ever been received for life membership; several committees have completed their work and have been discharged, and to new committees new work has been assigned; the Journal has been filled with valuable papers, and the demand upon its columns has been so great that its regular issue has been enlarged to 100 pages, and for the last three numbers a special edition of 150 pages has been authorized in order to make room for material that had accumulated in the hands of the Committee on Papers and Publications. The papers that have appeared in the Journal have been quite fully abstracted by other scientific periodicals both at home and abroad, and some of them have been reproduced entire. The address of the retiring president of the Society last year, Professor Charles E. Munroe, appeared in the journal *Science*, and the information therein contained was considered of such value that permission of its author was obtained to print it entire in the report of the Department of Agriculture of Ontario, Canada.

The changes in membership are as follows:

December 26, 1898, members.....	1298	
Associates .....	107	
Honorary .....	10	
Total .....	—	1415
New members qualified during year.....		219
		— 1634
Resigned.....	19	
Died .....	7	
Dropped from roll.....	39	
	—	65
		—
Dec. 26, 1899, members, 1430; associates, 131; honorary, 8; total		1569
The membership of the various local sections is:		
Rhode Island Section.....	27	
Cincinnati Section.....	67	
New York Section.....	361	
Washington Section.....	105	
Lehigh Valley Section.....	19	
Chicago Section.....	52	
Nebraska Section.....	16	
North Carolina Section.....	22	
Columbus Section.....	22	
North Eastern Section.....	232	
Philadelphia Section.....	97	
Michigan Section.....	35	
	—	
Total.....	1055	
Members not enrolled in any section.....	514	
Total membership, December 26, 1899.....	1569	
Per cent. of membership in local sections.....	67+	
“ “ “ “ not in local sections....	33—	

A few additional facts regarding the local sections may be of interest. *The Rhode Island Section*, territory the State of Rhode Island, headquarters, Providence, has held 8 meetings during the year at which papers were read and discussed. *Cincinnati Section*, territory a 75-mile radius from Cincinnati, except as specified, headquarters, Cincinnati, 8 meetings with papers, net gain of membership during the year, 25. *New York Section*, territory a 50-mile radius from New York City Hall, headquarters, New York City, 10 meetings, 45 papers presented by 35 different authors, net gain in membership during the year, 64. *Washington Section*, territory, District of Columbia, State of Maryland and the State of Virginia east of the 79th meridian, headquarters, Washington, 8 regular meetings, and three special, net gain in membership, 4. This section has also 30 local associates. *Lehigh Valley Section*, territory, that portion of the Lehigh Valley included between Easton and Mauch Chunk, headquarters, Lafayette College, Easton, and Lehigh University, South Bethlehem, 2 meetings, no change in membership. *Chicago Section*, territory, Chicago and suburbs, headquarters, Chicago, 7 meetings, gain in membership, 2. *Nebraska Section*, territory, the State of Nebraska, headquarters, Lincoln, 4 meetings, no change in membership. *North Carolina Section*, territory, the State of North Carolina, headquarters, Raleigh, 2 meetings, gain in membership, 7. *Columbus Section*, territory, a 75-mile radius from Columbus, except as specified, headquarters, Columbus, monthly meetings, gain in membership, 8. *North Eastern Section*, territory, the States of Maine, New Hampshire, Vermont, and Massachusetts, headquarters, Boston, Mass., 8 meetings, gain in membership, 32. *Philadelphia Section*, organized May 17, 1899, territory, a 60-mile radius from Philadelphia, except as specified, headquarters, Philadelphia, 2 meetings. *Michigan Section*, chartered December 7, 1899, territory, the State of Michigan, headquarters, the University of Michigan, Ann Arbor.

The present constitution has come into full operation during the past year. The council, as now constituted, will number 45 during the year 1900, composed of four members *ex-officio*, 12 past presidents, 17 representatives of Local Sections, and 12

councilors at large. The number of directors is 7, all of whom are members of the council.

During the past year the Committee on Papers and Publications has been enlarged to include representatives from the various departments of chemistry, making the total membership of the committee 10, the editor being chairman.

The final report of the Committee on Coal Analysis was presented at the Columbus Meeting, last summer, and the committee was discharged. This report has been sent to the Journal for publication.

The Committee on Duty-Free Importations, having already presented a highly satisfactory report, was also discharged at the Columbus meeting.

A Committee on Patent and Related Legislation, consisting of 25 members, with Charles E. Munroe as chairman, was appointed early in the year.

An International Committee on Atomic Weights has been appointed during the year to confer with similar committees from other national organizations in order to secure cooperation on the subject entrusted to the committee. The chairman of this committee is F. W. Clarke, whose annual report upon atomic weights has appeared regularly in the columns of the Journal during the past few years.

The only new life membership during the year is that of Charles E. Munroe, of Washington. We are encouraged, however, to expect others soon. The life membership fund now established in accordance with the constitution is set aside as a permanent investment, and it is to be hoped that this fund will rapidly accumulate in the near future.

The library of the Society is substantially housed on shelves in the rooms of the Chemists' Club, 108 W. 55th St., New York City. M. T. Bogert resigned as librarian during the year and A. A. Breneman was appointed acting librarian. Professor Breneman has done a great deal of work in putting the library in condition for use of the members, and his efforts have been highly appreciated by those who understand what has been accomplished. It is to be hoped that the society will soon be able to expend upon the library whatever is necessary to keep it in good condition, and to provide for its reasonable development.

Meanwhile, it is of interest to know that the trustees of the Chemists' Club in New York have voted to defray the expenses of a card catalogue for the library.

At the Columbus Meeting committees were appointed to draw up memorials with reference to the two honorary members of the society, Sir Edward Frankland and Professor Robert Wilhelm Eberhard Bunsen, who have died during the past year. The committee on Sir Edward Frankland reports at the present meeting, but the committee on the Bunsen memorial has deferred its report in order to obtain fuller information in regard to American chemists who have been pupils of Professor Bunsen. It is hoped that at least all members of the Society who have ever been his pupils, or have had any personal acquaintance with Professor Bunsen will forward without delay to the secretary of the Society any personal reminiscences and other matters of interest, including the names and addresses of any American chemists who have ever been in any way associated with Professor Bunsen.

A message of congratulation was sent by the president and secretary of the Society to Professor J. H. van't Hoff, one of our honorary members, upon the occasion of the celebration in Rotterdam on December 22, of the twenty-fifth anniversary of Professor van't Hoff's receiving the doctor's degree.

The record of the Society during the past decade, its present flourishing condition, and the outlook for the future, are cause for congratulation to every one who has at heart its welfare and its usefulness. Ten years ago its membership was but 205; to-day it is 1569, and we believe its influence and successful work has increased with even greater rapidity. Ever since its reorganization some ten or twelve years ago its growth has been rapid and vigorous, and under its wholesome and inspiring influence the chemists of America are, year by year, brought closer together in fraternal interest.

Respectfully,

ALBERT C. HALE, *Secretary.*

## REPORT OF THE TREASURER FROM MAY 1 TO DECEMBER 21, 1899.

NEW YORK, DECEMBER 21, 1899.

## RECEIPTS.

Balance from treasurer, Dr. McKenna.....	\$ 891 16
Received for dues from secretary.....	1175 00
Subscriptions .....	215 87
Received for back number.....	50
Received for advertising. ....	729 87
Received for interest, Knickerbocker Trust Co.....	1 35
Received for loan on special investment bond .....	1200 00
Received for interest on special investment bond.....	35 00
Received for interest on life-membership fund.....	36 60
	<hr/> \$4285 35

## DISBURSEMENTS.

For publication of Journal, 7 issues.....	\$1933 46
For reprinting January Journal .....	133 69
For author's reprints.....	133 42
For expenses, editor's office .....	27 54
For expenses, secretary's office (clerical) .....	403 83
For expenses, secretary's office (current) .....	197 85
For expenses, secretary's office (general) .....	426 15
For expenses, secretary's office, collection of dues .....	117 50
For expenses, library shelves .....	13 20
For expenses, treasurer's office.....	22 14
For expenses, New Haven Meeting .....	11 00
For expenses, general.....	42 49
For expenses, rebate on subscription .....	4 00
For advertising .....	1 76
For emigrant savings bank .....	36 60
For rebate to local sections as follows :	
Cincinnati.....	\$ 88 33
Columbus .....	30 00
New York.....	200 00
North Eastern.....	30 00
Philadelphia.....	100 00
	<hr/> \$ 448 33
Balance in Knickerbocker Trust Co., Dec. 21, 1899..	332 39
	<hr/> \$4285 35
Unpaid bills, editor's salary.....	\$250 00
Unpaid bills, treasurer's services .....	150 00
	<hr/>
Total.....	\$400 00

A. P. HALLOCK, *Treasurer.*

Accounts examined and found correct, E. &amp; O. E.

WM. MCMURTRIE,  
J. H. WAINWRIGHT,  
ELWYN WALLER,  
*Finance Committee.*

## ASSETS.

Special investment fund (\$2000, 2½ per cent. N. Y. gold bond, due 1915).....	\$2097 50
Life membership fund (\$1000, 3½ per cent. N. Y. gold bond, due 1925).....	\$1080 38
Emigrant savings bank.....	219 62
	<hr/>
	1300 00
Balance in Knickerbocker Trust Co .....	332 39
Cash in secretary's hands.....	41 39
Cash in librarian's hands .....	45 39
Dues unpaid, 1898 .....	235 00
Dues unpaid, 1899 .....	740 00
Uncollected accounts, editor's office.....	1225 50
	<hr/>
	\$6017 17

## LIABILITIES.

Loan on special investment bond .....	\$1200 00
Editor's salary.....	250 00
Treasurer's services .....	150 00
Life members.....	1300 00
Balance on actual assets.....	3117 17
	<hr/>
	\$6017 17

## ACTING LIBRARIAN'S REPORT FOR 1899.

NEW YORK, December 23, 1899.

*To the Council of the American Chemical Society :*

GENTLEMEN—The library of the Society has been in my charge, as acting librarian, since May 16th of the present year. It is now arranged in the library room of the Chemists' Club. The collection is largely made up of chemical periodicals, in sets more or less complete, but largely unbound. To put it into shape for convenient use it is imperative that much binding should be done and that the incomplete sets should be filled up. A catalogue should also be made. No money has been available for these purposes, and I hereby renew my previous suggestion to the council that an appropriation of \$200 be made for binding, and in addition recommend that the sum of \$500 be applied during the coming year to the purchase of missing numbers of periodicals already represented in the library.

By the action of the trustees of the Chemists' Club, recently taken, the expense of preparing a card catalogue will be assumed by the club. A printed catalogue for the use of members at a distance should be provided for by the Society. I would suggest that the council consider, as soon as possible, the question of de-



fining the plan upon which the library shall be built up. At present it has a large quantity of material which is of very remote interest to chemists, and the care of this adds materially to time and expense required in the work of the library. It seems to me that this library should be a chemical library first of all. With the means and influence of the American Chemical Society it may be made one of the best chemical libraries in the country—perhaps in time the best—but it can only fulfil its purpose by means of some reasonable system of limitation or exclusion which shall avoid the accumulation of other matter, which general libraries can much better supply. As the library is likely always to be located in one of the large cities where general library facilities are abundant, the propriety of making it strictly a library for chemists is the more apparent.

The financial affairs of the library have been reported to the treasurer of the Society, and will appear in his annual statement.

Very respectfully,

A. A. BRENNEMAN, *Acting Librarian.*

#### REPORT OF THE EDITOR FOR 1899.

*To the Members of the American Chemical Society :*

It is surely not necessary to announce to the world that we have in the space of seven or eight years grown into a vigorous, lusty Society. This meeting especially offers evidence of the union of the best American chemists in our effort.

It is a matter of great rejoicing to those of us who have been pulling in the traces so long, doing the best we could with material sometimes unpromising, that the best of the profession have one by one come to our aid and that we are rapidly approaching the goal.

When I became editor in 1893 there were two papers ready for publication and five numbers of the Journal in arrears. This had come to pass through the process of reorganization. Since that time progress has been steady and of late years rapid.

At the Columbus Meeting the council took what is generally considered a great step in advance in increasing the size of the Publication Committee. This increase in numbers has several advantages.

First. Most papers may be published at once after reference to only one member particularly versed in the portion of chemistry covered by the paper.

Second. The number of papers referred to each member is decreased, decreasing the individual burden and increasing the chance of careful consideration and wise, helpful suggestion.

The committee intends to use material of value from every available source. The effort will be made to weed out redundancies and to pay some attention to the manner of statement as well as to the matter contained. It is our intention to offer only helpful criticism to the authors of papers with a desire for their cooperation in making the pages of the Journal a proper reflection of American progress in chemistry.

Two factors seem to be needed in this work: First, cordial cooperation from contributors to the Journal; and second, proper financial support. Both of these seem now assured.

An index to the first twenty volumes has been prepared and will shortly be published.

At this meeting of the council the editor will propose that a committee be constituted to investigate the question of what is the best book-paper for our use and to make recommendations concerning it.

In conclusion it may not be uninteresting to summarize here what has been done since I became editor. In 1893 the Journal contained 98 papers, with a total of 720 pages. In 1894 there were 16 pages of proceedings and 152 papers, covering 891 pages, a total of 907 pages. In 1895 there were 72 pages of proceedings and 145 papers, covering 1010 pages, a total of 1082 pages. In 1896 we printed 126 pages of proceedings and 142 papers, covering 1124 pages, a total of 1250 pages. In 1897 we printed, for the first time, a Review of American Chemical Research, 210 pages, proceedings 66 pages, and 124 papers, covering 966 pages, a total of 1242 pages. In 1898 there were 182 pages of review, 106 pages of proceedings, and 126 papers, covering 999 pages, a total of 1289 pages. This year we have printed 157 pages of review, 106 pages of proceedings, and 135 papers, covering 1187 pages, a total of 1450 pages. During this period the edition has been increased from 750 to 2000 copies. Of the November, 1899, issue, 1679 copies were sent out. With the steady

increase of membership, which still keeps up, we shall probably have to still further increase the edition for 1901.

EDWARD HART, *Editor*.

#### REPORT OF THE COMMITTEE ON MEMBERSHIP.

*To the Council of the American Chemical Society :*

GENTLEMEN—Your Committee on Membership desires to report one of the most successful years in the history of the Society in the acquisition of members. The total number of nominations passed upon by the committee is 256, of which 226 are active, and 30 associate members. While two special influences may be noted, namely, the formation of a Michigan Section and the meeting now in progress in New Haven, it will nevertheless be seen from the following statement how natural, steady, and healthful has been our growth.

January, 46 ; February, 21 ; March, 30 ; April, 11 ; May, 20 ; June, 8 ; July, 4 ; August, 7 ; September, 11 ; October, 23 ; November, 34 ; December, 41.

While congratulating the Society on this prosperity, your committee feels that our efforts must in no way be relaxed as with a still larger membership, a wider scope can be given the Society and a greater usefulness to the Journal.

It has been suggested by several of the most active members at work in securing the interest of students in the work of the Society that the interests of all would be better subserved if students elected to associate membership should be advanced to full membership on the simple forwarding of their credentials of graduation. This would obviate the necessity of a new form being made out and passed through the routine of the committee.

Respectfully submitted,

CHARLES A. DOREMUS, *Chairman*,  
A. A. BRENNEMAN,  
PETER T. AUSTEN.

#### REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.

December 1, 1899.

*To the American Chemical Society :*

Your Committee on international action relative to a uniform system of atomic weights begs to submit the following report of progress :

It has communicated with several foreign organizations: namely, the German, English, and Belgian chemical societies. At our request the English society has appointed a committee upon the subject; and in the chemical section of the British Association, at its recent meeting, the proposition for international action was somewhat discussed, a letter from the chairman of this committee being the basis for discussion. The attitude of the English organizations towards the plan for an international conference, is altogether favorable; that of the other societies is not definitely stated. The Belgian society has formally adopted the table of atomic weights issued last year by the German committee, and several other local organizations in Europe have done the same thing.

In our conferences various questions have arisen as to nomenclature, standards and methods of stating results. On these subjects no present action is recommended, partly because of differences of opinion, and partly because final action could be of weight only when agreed to by all leading chemical societies. For us to act now would savor too much of forestalling the desired international decisions. Neither do we recommend the adoption of any specific tables of atomic weights, for three such tables, which are fairly in agreement, are now proposed; and a fourth table would only lead to confusion. The tables of the German committee, of Clarke, and of Richards are all more or less in use; and although the differences between them are minor, their reconciliation should be effected by the larger body of experts which will probably be formed.

The Congress of Chemists which will meet in Paris in July next, seems to afford the best opportunity for a general discussion of the subject; not only as to the values to be adopted, but also as to the best method for clearing up outstanding uncertainties in our constants. Your committee therefore offer the following recommendations:

First, that the officers of the above-mentioned Congress be requested to invite a joint meeting of all international committees upon atomic weights, to be held during the Congress in July, 1900, and under its auspices.

Second, that the joint committee so formed shall have power to add to its membership.

Third, that the American Chemical Society shall invite the cooperation of other organizations in the United States. The American Academy of Arts and Sciences has already appointed a committee, consisting of Professors T. W. Richards, Wolcott Gibbs, and Ira Remsen, a committee with which we should act in harmonious relations.

Very respectfully,

F. W. CLARKE, *Chairman.*

J. W. MALLET.

EDWARD W. MORLEY.

THEO. W. RICHARDS.

EDGAR F. SMITH.

#### REPORT OF COMMITTEE ON PRIESTLEY MEDAL.

WASHINGTON, D. C., December 16, 1899.

*Dr. Edward W. Morley, President American Chemical Society:*

SIR:—Your committee, to which was referred the consideration of the motion, “That on the twenty-fifth anniversary of the establishment of the Society, a medal be given to that chemist who, in the opinion of the council, has made the most valuable contribution to chemical knowledge during the current year, and further, that the medal be called the ‘Priestley Medal’,” begs to report that it deems it inadvisable for the society to found a medal from funds obtained from dues of members, since in its judgment medals and prize funds should be independently acquired for the specific purposes named by the donors.

Your committee recommends that some recognition be made of the twenty-fifth anniversary of the founding of the Society, which will occur on April 6, 1901, and it suggests that provision be made for a special memorial address, and that a statement of what the Society has accomplished to that date be published, and issued to all the chemists in America.

Respectfully submitted,

CHARLES E. MUNROE, *Chairman.,*

J. W. MALLET,

ALBERT B. PRESCOTT.

*Committee.*

**BOARD OF DIRECTORS.****MINUTES OF THE MEETING OF THE BOARD OF DIRECTORS,  
DECEMBER 28, 1899.**

At the close of the meeting of the council in the Kent Chemical Laboratory, New Haven, President Morley called the Board of Directors to order. There were present Messrs. Morley, Hale, Hallock, Dudley, and McMurtrie.

Upon motion duly seconded and carried, the directors authorized the appropriation of the funds recommended by the various motions approved by the council at the session just closed.

There being no further business, the board then adjourned.

ALBERT C. HALE, *Secretary*.

**COUNCIL.****MINUTES OF THE COUNCIL OF THE AMERICAN CHEMICAL  
SOCIETY, DECEMBER 28, 1899.**

The council was called to order at 2.10 P.M., in the Kent Chemical Laboratory, New Haven, Conn., President Edward W. Morley in the chair.

There were present Messrs. Morley, McMurtrie, Hale, Hart, Catlin, Wiley, Hillebrand, Johnson, Clarke, Marshall, Gooch, Smith, Sabin, Love, Hallock, Alden, Long, Munroe, Talbot, Dudley, Prescott, and Wells.

The minutes of the council, as recorded in the secretary's book up to date, were approved.

It was voted that all nominees for membership, up to the close of this meeting, be considered as acted upon by the council, and the secretary shall declare them elected whenever all the other requirements of the constitution, in regard to them as nominees, shall have been met.

Dr. Hart reported progress for the "Committee on Exchanges" and Dr. Dudley for the "Committee on Abstracts and Reviews."

A report was presented by the committee appointed to consider a plan for celebrating the twenty-fifth anniversary of the founding of the Society, by awarding a medal for the "most valuable contribution to chemical knowledge," etc. The committee reported adversely upon the question of the medal but recommended a plan for celebrating the twenty-fifth anniversary of the

**Society.** The report was accepted and its recommendations adopted.

It was voted that hereafter, at the annual meeting of the council, nominations shall be made for the ensuing year, to fill the various offices and committees, the incumbents and members of which are to be elected by the council, in accordance with the constitution.

Upon motion of Professor Clarke, the following was adopted :

*Resolved*, That the officers of the council for the coming year shall be nominated by ballot ; if for any office a nominee shall receive a majority of the votes cast, he shall be declared to be elected to said office ; in other cases, the names of the three nominees having the highest number of votes shall be referred to the council for further balloting.

It was voted that publication in the Journal of the Society, of any action of the council, shall be considered as sufficient notice to the councilors that such action has been taken.

It was voted that the next general meeting of the society shall be held on Monday and Tuesday, June 25 and 26, in connection with the meeting of Section C of the A. A. A. S.

The report of the Finance Committee was presented and the following recommendations were adopted :

1. At the general annual meeting, each officer shall submit a schedule comprising his estimated expenses, in detail, for the coming year.

2. After all such estimates shall have been submitted, the council shall prepare a budget of expenses and the directors shall, upon the recommendation of the council, apportion the funds of the Society, or so much thereof as may be necessary, in accordance therewith.

3. All officers of the Society, who shall in any manner collect or receive moneys from any source, shall transmit the same monthly to the treasurer with a statement of the source or sources from which such receipts are collected.

4. All disbursements on account of the Society shall be made only by the treasurer upon vouchers duly approved by the Finance Committee, after having been checked by the officer by whose account the disbursement is made ; and the treasurer shall, in keeping his accounts, charge every disbursement to

some one of the several appropriations made by the directors in accordance with the preceding recommendations.

The following recommendation of the Finance Committee was referred to the various local sections of the Society for the expression of opinion thereon: "In regard to the apportionment of the Society's funds for the benefit of local sections, the Finance Committee believe, and earnestly recommend, that the following system would be preferable to the one at present in force; *viz.*, that when the local membership of the section is below fifty (50) that section shall be entitled to draw annually an amount equivalent to one-third of the aggregate dues paid to the Society by its members. If the membership shall exceed 50 and be less than 200 the section shall be entitled to draw one-fourth; and if it shall reach a total of 200 the section shall be entitled to draw one-fifth."

The following suggestion was referred back to the Finance Committee after a number of the councilors had expressed themselves adversely in regard to it: In regard to the general manner of conducting the business of the Society the committee are strongly of the opinion that it would be extremely desirable and would result in a very decided economy to employ for that purpose a business manager at a reasonable salary; to turn over to him all the details connected with its administration comprising the actual keeping of all accounts, the details of correspondence, etc., etc., and to locate the Society's business at some central office.

The report of the Committee on Library Appropriations was received and placed on file, also the report and recommendations of the acting librarian.

On motion of Dr. McMurtrie it was voted that \$400, or so much thereof as may be necessary, be and the same is hereby appropriated for the binding of unbound material in the library and the completion of sets, and that \$100, or so much thereof as may be necessary, be and the same is hereby appropriated to pay for clerical services of the librarian.

On motion of Dr. Munroe it was voted "that it is the sense of the council that the phrase 'which shall be held in perpetuity to guarantee the future interests of such life members,' in Section 2, Article X, of the constitution, means that the income from



each life membership fee shall, during the life of the member who paid this fee, be turned into the treasury to be used in meeting the general expenses of the Society just as the annual dues of members are now used."

It was resolved that Dr. Marcus Benjamin and the editor be appointed a Committee on Portraits for the Journal. It was voted that a Committee on Paper to be used in the Journal, be appointed, consisting of three members, of which the editor shall be *ex-officio* chairman. (By subsequent vote of the Council this committee was increased to five, consisting of the following persons: Edward Hart, chairman, Henry Carmichael, A. D. Little, M. L. Griffin, and C. B. Dudley.)

It was voted that the editor be authorized to cause to be printed sample pages of the December issue, including the cover, the advertising pages, the annual table of contents, and one signature of reading matter, the whole to be used for advertising purposes.

The committee appointed to attend the Pure Food and Drug Congress held in Washington, D. C., January 8 to 20, reported that it had performed the duties assigned it and that nothing was accomplished by the Congress. The report was accepted and the committee discharged.

Upon motion by Dr. Wiley the thanks of the Society, through the council, were extended to the retiring president for the able direction of the affairs of the Society during the past year.

W. F. Hillebrand submitted the following amendments to the by-laws: Substitute for Section 17, "The Journal of the Society shall not be sent to members or associates until after the receipt of their dues for the current year.

"The secretary shall have the above printed on his annual notification that dues are payable, and shall call the attention of delinquent members to it at least once every three months."

Amend Section 20 by substituting for the first sentence the following: "The Secretary shall give written notice to the editor, immediately before the mailing of the first annual number of the Journal, of all persons in arrears, in order that the provisions of the by-laws regarding such cases may be carried into effect."

The Council then adjourned.

ALBERT C. HALE, *Secretary.*

The following named officers were elected by the Council January 30, 1900 :

*Secretary*—Albert C. Hale.

*Editor*—Edward Hart.

*Treasurer*—Albert P. Hallock.

*Librarian*—E. G. Love.

*Director*—Charles F. Chandler.

*Members of Committee on Membership*—Charles A. Doremus, A. A. Breneman, Peter T. Austen.

*Members of Finance Committee*—Elwyn Waller, J. Howard Wainwright.

*Members of Committee on Papers and Publications*—Edward Hart, Editor, *Chairman*, H. N. Stokes, W. A. Noyes, H. P. Talbot, A. A. Noyes, H. W. Wiley, Wm. McMurtrie, W. F. Hillebrand, John H. Long, and Edgar F. Smith.

In view of the fact that the number of pages in the December issue of the Journal (because of the extent of the index and the Review of American Chemical Research) unavoidably exceeded the limit of 150 pages ordered by the council, the treasurer was authorized by council to pay for the entire issue at the rates prescribed in the contract.

A Committee on Paper to be used in the Journal, consisting of three members, was authorized at the New Haven meeting of the Council. On January 30, 1900, authority was given the president to increase the number of members of this committee to five.

The Council has directed that persons who as undergraduates have been elected associates shall be declared to be members upon graduation from the chemical course of any institution of recognized standing.

#### NAMES PROPOSED FOR MEMBERSHIP.

Armsby, Prof. H. P., State College, Pa.

Arnott, George W. Campbell, 27 William St., N. Y. City.

Bach, August, 537 Nelson St., Chicago, Ill.

Bullard, Frank D., 245 Bradbury Block, Los Angeles, Cal.

Douglas, William, Plantation Diamond, Demerara, British Guiana.

Goodell, Geo. A., 284 St. Nicholas Ave., N. Y. City.

Hamlin, Addison, 25 5th St., Bangor, Me.

Hulett, Geo. A., 706 S. Thayer St., Ann Arbor, Mich.

Mills, James E., Chapel Hill, N. C.

Mork, Harry S., 21 Wabeno St., Roxbury, Mass.  
Norris, Robert Stewart, Santa Maria, Cal.  
Remington, Joseph P., 1832 Pine St., Philadelphia, Pa.  
Richards, Joseph, 1802 Catherine St., Philadelphia, Pa.  
Richardson, William Derrick, 4803 Madison Ave., Chicago, Ill.  
Ross, Herbert W., 1070 16th St., Oakland, Cal.  
Syme, W. A., Raleigh, N. C.  
Thorne, Ernest E. H., Bridgeton, Barbadoes, B. W. I.  
Thurlow, Nathaniel, 55 New St., Newark, N. J.  
Weld, Fred. C., Littleton, Mass.  
Wolfe, J. V., Jr., Rochester, Mich.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Bates, Hugh H., 502 E. 3d St., Cincinnati, Ohio.  
Berghausen, Oscar, 644 Crown St., Walnut Hills, Cincinnati,  
Ohio.  
Black, Jesse A., Poly. Inst., Worcester, Mass.

NEW MEMBERS ELECTED JANUARY 30, 1900.

Archibald, Eben H., 109 Ellery St., Cambridge, Mass.  
Ballard, J. Clarence, U. S. Expt. Station, Lafayette, Ind.  
Behr, Gustave E., Jr., 1256 Massachusetts Ave., Cambridge,  
Mass.  
Black, Otis F., 10 Avon St., Cambridge, Mass.  
Bonnet, Frederic, Jr., 13 Mellen St., Cambridge, Mass.  
Cohoe, Wallace P., 14 Boylston Hall, Cambridge, Mass.  
Colhane, Daniel F., 58 Moore St., Cambridge, Mass.  
Dailey, J. Glanding, care Carpenter Steel Co., Reading, Pa.  
Davis, Robert S., 1330 12th Ave., Altoona, Pa.  
Downey, James E., 10 Taylor St., Holyoke, Mass.  
Earle, Richard B., 403 Craigie Hall, Cambridge, Mass.  
Hale, William J., 42 Kirkland St., Cambridge, Mass.  
Havens, Franke S., 9-13 Mercer St., N. Y. City.  
Kittredge, Harvey G., Dayton, O.  
Krebs, H. J., Wilmington, Del.  
MacIntosh, Douglas, 208 E. 61st St., N. Y. City.  
Sandford, Wm. E., Kewanee, Ill.  
Sanger, Charles R., Chem. Lab., Harvard College, Cam-  
bridge, Mass.  
Schaak, Milton F., 108 Penn St., Brooklyn, N. Y.  
Williams, Simon E., Boylston Hall, Cambridge, Mass.

NEW MEMBERS ELECTED FEB. 13, 1900.

Alexander, Jerome, 502 W. 45th St., N. Y. City.  
Jandrier, Edmond, Peace Dale, R. I.

## ASSOCIATES ELECTED FEBRUARY 13, 1900.

Craig, Archibald G., 5516 Graham Place, Pittsburg, Pa.  
 Gearing, James H., 2111 Sidney St., Pittsburg, Pa.  
 Stifel, Walter H., 1319 Locust St., Allegheny, Pa.  
 Waters, Oliver G., 223 5th Ave., Pittsburg, Pa.  
 Wells, Allan, 213 S. St. Clair St., Pittsburg, Pa.

## CHANGES OF ADDRESS.

Adgate, Matthew, care General Chem. Co., Syracuse Works, Syracuse, N. Y.  
 Anderson, Duncan, Jr., 104 8th St., Roanoke, Va.  
 Behr, Arno, Arlington Court, Pasadena, Cal.  
 Burwell, A. W., 208 Superior St., Cleveland, Ohio.  
 Cairns, Fred. I., Anaconda, Mont.  
 Davis, Wm. Walley, care Va. Iron, Coal and Coke Co., Bristol, Va.-Tenn.  
 Enequist, John, 556 Greene Ave., Brooklyn, N. Y.  
 Escher, Paul, care Acker Process Co., Niagara Falls, N. Y.  
 Field, Chas., 3d, 1747 Lawrence St., Denver, Col.  
 Fischer, Robert, 208 Stewart Ave., Ithaca, N. Y.  
 Fleck, Herman, Belleville, N. J.  
 Foster, John, Sheffield, Ala.  
 Given, Arthur, 1 Plympton St., Worcester, Mass.  
 Hartman, Wm. E., Kalamazoo Gas Works, Spring and Pitcher Sts., Kalamazoo, Mich.  
 Kelley, John H., care Tenn. Phosphate Co., Ridley, Maury Co., Tenn.  
 Kelly, F. G., Chapel Hill, N. C.  
 Lorenz, H. W. F., Univ. of Pa., Philadelphia, Pa.  
 Ludlow, Gabriel, Box 344, Wilmington, N. C.  
 Miller, F. W., Talladega, Ala.  
 Miller, Hugh L., 24 Broad St., Charleston, S. C.  
 du Pont, P. S., The Johnson Co., Lorain, Ohio.  
 Schoen, Joseph, care Standard Syrup Ref. Co., 12 S. Commercial St., St. Louis, Mo.  
 Simons, Frank D., "The Montrose Flats," 1115 9th St., Washington, D. C.  
 Small, Fritz H., care Graton & Knight Mfg. Co., Worcester, Mass.  
 Smith, Frederic J., Box 46, Elizabeth, N. J.  
 Thorburn, A. D., Room 200, 100 State St., Chicago, Ill.  
 Twitchell, E., Wyoming, Ohio.

## ADDRESS WANTED.

Wolff, Frank A., Jr., formerly Columbia Univ., N. Y. City.

## MEETINGS OF THE SECTIONS.

## CINCINNATI SECTION.

The 72nd regular meeting was held on Friday, December 29, 1899, in the Auditorium of Hanna Hall, University of Cincinnati, with about 150 persons in attendance.

Dr. Alfred Springer presented the subject: "A Trip through the Yellowstone Park" beautifully illustrated by a great number of photographic lantern-slide views.

The meeting was then resumed in the Chemical Lecture Room, with 26 members present, and President Simonson in the chair. Dr. Thomas Evans made a preliminary report on ricinine. After the reading of the reports of officers for the past year, the election of officers for 1900 was held, resulting in the following ticket:

*President*, Thomas Evans; *Vice-presidents*, Hannah L. Wessling, Raymond M. Hughes; *Secretary*, Frank I. Shepherd; *Treasurer*, Henry B. Foote; *Executive Committee*, B. M. Pilhashy, Otto Dieckmann, Fred. Homburg; *Representative in the Council*, Alfred Springer (elected at the November meeting).

The following chairmen of standing committees were elected:

*On Papers and Publications*, Frank I. Shepherd; T. H. Norton and E. Twitchell, associate members; *On Didactic, Physical, and Inorganic Chemistry*, T. H. Norton; *On Organic Chemistry*, Thomas Evans; *On Analytical Chemistry*, Wm. Simonson; *On Medical, Physiological, and Biological Chemistry*, Wm. H. Crane; *On Technical and Pharmaceutical Chemistry*, J. Everhard Weber.

Upon motion, the meeting adjourned.

S. WALDBOTT, *Secretary*.

## PHILADELPHIA SECTION.

The meeting was called to order in the Harrison Laboratory, University of Pennsylvania, December 21, 1899, at 8.20 P.M., by the presiding officer, 35 members and visitors being present.

Prof. George F. Barker presented the paper of the evening "Some Recent Progress in Physics." He called attention to the method employed to measure the wave-lengths of some extremely high-pitched notes.

He also showed the spectrum of the new gas neon which was

prepared by Prof. Dewar and samples of the newly discovered substance radium which emits rays similar to the X-rays.

The meeting adjourned at 9.50 P.M.

F. E. DODGE, *Secretary*.

#### WASHINGTON SECTION.

The regular meeting was held on December 14, 1899.

The first paper of the evening was read by Dr. W. D. Bigelow and was entitled "Determination of Metals in Canned Goods," by W. D. Bigelow and L. S. Munson.

After an examination of a number of the methods most commonly employed the authors gave preference to a modification of Allen's method.

The entire contents of the can are thoroughly mixed, and 75 to 100 grams taken for analysis. Often it is found preferable to dry the entire sample, extract with petroleum ether, again dry and grind, to obtain a permanent sample. In this case only 25 grams are employed in the determination of metals.

In either case the sample taken is treated with 4 cc. of strong sulphuric acid, 2 cc. of nitric acid, and 3 grams of magnesia. The whole is heated on a water-bath until it becomes pasty. It is then ignited over a Bunsen burner or in a muffle-furnace until thoroughly charred, ground in a mortar, again ignited to complete combustion, nitric acid being added from time to time towards the close of the operation. The residue is then boiled for a half hour in about 40 cc. of dilute hydrochloric acid (1 : 3), almost neutralized with sodium hydroxide, precipitated with hydrogen sulphide and filtered. The precipitate is dried and thoroughly mixed with 1 gram each of sodium carbonate, potassium carbonate and sulphur, fused for one-half hour in a covered porcelain crucible, digested in water and filtered.

The insoluble portion contains copper and lead. It is dissolved in nitric acid, and divided into two equal portions, in one of which the lead is precipitated as chromate and in the other copper is determined by titration with potassium cyanide. The filtrate from the fused sulphides is acidified with acetic acid, filtered and the precipitate thoroughly washed and transferred together with the filter-paper to a solution of ferric chloride, which is heated to the boiling-point and titrated with potassium bichromate. Zinc is precipitated as sulphide in the filtrate from

the original sulphide precipitate, after adding acetic acid and neutralizing the mineral acid with sodium hydroxide.

The second paper of the evening was read by Dr. Fireman, and was entitled: "The Action of Ammonium Chloride upon Tetra- and Pentachlorides" (preliminary communication), by P. Fireman and E. G. Portner.

The last paper of the evening was read by Mr. J. D. Tinsley and was entitled: "On the Estimation of the Water-soluble Constituents of Soils," by J. D. Tinsley and F. K. Cameron.

Dr. Seaman spoke on the size of medicine droppers found in the market. He had found them very variable, giving drops of different sizes. He showed that the size of the drop depends on the external diameter of the orifice and not on the thickness of the walls.

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The regular meeting was held on January 11, 1900. The following officers were elected for the ensuing year: *President*, Dr. H. C. Bolton; *Vice-presidents*, Mr. V. K. Chesnut and Dr. Peter Fireman; *Secretary*, Mr. William H. Krug; *Treasurer*, Mr. W. P. Cutter; *Executive Committee*: The above officers and Messrs. Wirt Tassin, E. E. Ewell, H. N. Stokes, F. K. Cameron, and W. F. Hillebrand.

WILLIAM H. KRUG, *Secretary*.

#### NEW YORK SECTION.

The regular meeting of the New York Section was held at the Chemists' Club, 108 West 55th street, on Friday evening, January 5th, Dr. C. F. McKenna, presiding.

In addition to the program announced, Prof. George F. Barker was the unexpected guest of the section. He exhibited a sample of "Radio-active Substance A"; also, some photographs made by the same on sensitized plates, which had been wrapped in three thicknesses of orange-yellow paper, and as many thicknesses of black paper over them. Prof. Barker gave a brief historical sketch of the work done on this compound, bringing the subject up to date. The room was darkened to enable the audience to observe the feeble luminosity of the substance.

The regular program was then proceeded with and the following papers were read: "Laboratory Method for the Continuous and Uniform Generation of Acetylene and its Purification," by J. A. Mathews; "Upon the Carbide of Gold," by J. A. Mathews and L. L. Watters; "On the Reactions of Alkalies with the Cellulose Nitrates," by C. W. Volney; exhibition of lantern slides illustrating "Filters for Purifying Public Water Supplies," by Allen Hazen.

DURAND WOODMAN, *Secretary*.

#### LEHIGH VALLEY SECTION.

A regular meeting of the Lehigh Valley Section was held at Easton, Pa., in the Chemical Laboratory of Lafayette College, on Thursday evening, January 18th. Presiding Officer Richards was in the chair and eighteen members and invited guests were present. The following papers were read: "The Action of the Weaker Organic Acids on Carbonates," by Joseph W. Richards and Norman S. Powell; read by Mr. Powell. "An Abrasion Test for Emery," by Porter W. Shimer. "Goldschmidt's New Apparatus for Cutting Crystal Models," by Joseph W. Richards. "A Method for Determining Zinc by the Use of Standard Thiosulphate Solution," by Richard K. Meade.

RICHARD K. MEADE, *Secretary*.



# Proceedings.

## COUNCIL.

In view of the U. S. Treasury decision 21170 relative to free importation of philosophical apparatus and preparations, which is likely to affect seriously the work of educational institutions and the laboratories of research, the council has voted that the president of the Society be authorized and directed to appoint a committee consisting of fifteen members of the Society, who shall be instructed to consider the present status of the laws and regulations governing the free importation of instruments, apparatus, and materials used in research work, and to take such action in the premises in the direction of securing such new legislation or modifications of existing laws and regulations as they may find necessary to the interests of the educational and research institutions.

The council has also voted that the president be authorized to appoint from the membership five persons to represent the Society in the Fourth Congress of Applied Chemistry, and that the sum of one hundred francs, or the equivalent thereof, be and is hereby appropriated for a subscription from the Society to the expenses of the said congress.

The following named persons have been elected by the council to the offices mentioned :

Charles F. McKenna, counoilor for term expiring December, 1901.

Ernest E. Smith, director for term expiring December, 1901.

John A. Mathews, member of Finance Committee.

## NAMES PROPOSED FOR MEMBERSHIP.

Carveth, Hector R., Chem. Lab., Cornell Univ., Ithaca, N. Y.

Cratty, John M., Chem. Lab., Navy Yard, Norfolk, Va.

Davies, Charles T., 1412 Perkiomen Ave., Reading, Pa.

Dunn, Willis A., 736 Fifth Ave., Helena, Mont.

Griffith, Herbert E., Galesburg, Ill.

Hooker, Samuel C., Spreckels Sugar Ref., Philadelphia, Pa.  
 McFarland, Wm. S., Barrett Mfg. Co., Philadelphia, Pa.  
 Mork, Harry S., 21 Wabeno St., Roxbury, Mass.  
 Norris, Robert S., Santa Maria, Cal.  
 Rosentwist, Birger G. A., Fessenden St., Jamaica Plain,  
 Boston, Mass.  
 Ross, Herbert W., 1070 16th St., Oakland, Cal.  
 Smith, Fred D., Missoula, Mont.  
 Starz, Emil, 204 N. Rodney St., Helena, Mont.  
 Syme, W. A., Raleigh, N. C.  
 Taylor, H. W., Lab. Tenn. Cotton Oil Co., Memphis, Tenn.  
 Whittier, Charles T., Provident Chem. Wks., St. Louis, Mo.

#### NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Burke, Edmund, Bozeman, Mont.  
 Clark, Clara, Bozeman, Mont.  
 Cockrill, Irwin, Bozeman, Mont.  
 Draper, Charles W., Bozeman, Mont.  
 Evans, James A., 110 N. Thayer St., Ann Arbor, Mich.  
 Lamme, Maurice, Bozeman, Mont.  
 Reese, Herbert J., Bozeman, Mont.  
 Spragg, Frank A., Bozeman, Mont.  
 Wood, Jas. Leslie, Jr., Bozeman, Mont.

#### CHANGES OF ADDRESS.

Adams, Isaac, 1776 Massachusetts Ave., N. Cambridge, Mass.  
 Austin, N. M., 1236 Pennsylvania Ave., Allegheny, Pa.  
 Bassett, W. H., N. J. Zinc Co., Newark, N. J.  
 Baxter, Wm. T., 254 New York St., Aurora, Ill.  
 Beck, Oscar C., 305 S. 40th St., Philadelphia, Pa.  
 Becker, J. B., 1104 Douglass St., Sioux City, Iowa.  
 Clarke, Thomas, Birmingham, Ala.  
 Couch, Guy E., 631 E. Front St., Cincinnati, Ohio.  
 Crane, Frederic, 28 Hillside Ave., Montclair, N. J.  
 Gabriel, Geo. A., Box 390, Cumberland Mills, Me.  
 Hall, C. A., 3220 Powelton Ave., Philadelphia, Pa.  
 Harding, E. P., 22 Landhaus Strasse, Heidelberg, Germany.  
 Henderson, W. E., Ohio State Univ., Columbus, Ohio.  
 Johnson, E. S., 315 Highland Ave., Syracuse, N. Y.  
 Keller, Edward, P. O. Box 724, Baltimore, Md.  
 Kelly, F. G., care Tenn. C. I. & R. Co., Birmingham, Ala.  
 Lyng, M. H., Republic, Wash.  
 Mason, Francis P., 214 Monadnock Bldg., Chicago, Ill.  
 Miller, F. W., Talladega, Ala.  
 McBryde, J. B., Blacksburg, Va.  
 Perkins, Albert S., 75 Milton Ave., Hyde Park, Mass.

Peyton, Wm. C., Peyton Chem. Wks., Mutual Life Bldg., San Francisco, Cal.

Reese, Chas. L., N. J. Zinc Co., Newark, N. J.

Seidensticker, L. J., 178 Thornton St., Boston, Mass.

Shilstone, Herbert M., 166 St. James Place, Brooklyn, N. Y.

Smolt, F. O., 23 N. Tejon St., Colorado Springs, Col.

Sy, Albert P., 24 High St., Buffalo, N. Y.

Thomas, W. H., care Colonial Bleaching & Printing Co., St. Henry, Montreal, Can.

Torrey, Chas. A., Jr., 1015 S. 48th St., Philadelphia, Pa.

Wolff, Frank A., Jr., Columbian Univ., Washington, D. C.

Worstall, Robert A., 139 Kennard St., Cleveland, Ohio.

#### ADDRESSES WANTED.

Hartman, Wm. E., 843 Lafayette Ave., Detroit, Mich.

Wood, J. R., 439-441 Green St., Philadelphia, Pa.

#### CORRESPONDENCE.

The following is the copy of a letter received by ex-President Morley from Dr. J. H. van't Hoff, in response to the Society's cablegram:

CHARLOTTENBURG, January 27, 1900.

*My Dear Colleague:*

I beg you to express my feelings of thankfulness to the American Chemical Society, which gladdened and honored me by its telegraphic congratulations on my jubilee. At the same time I have to thank you and the secretary, Mr. Hale, more especially, the congratulation having your names. With my best wishes for the prosperity of your Society, I am,

Yours truly,

J. H. VAN'T HOFF.

#### MEETINGS OF THE SECTIONS.

##### CINCINNATI SECTION.

The seventy-third regular meeting of the Cincinnati Section was held in the Chemical Lecture Room of Hanna Hall, University of Cincinnati, on Monday evening, January 15, 1900. President Evans occupied the chair. Twenty-five members were present.

Dr. Otto Dieckmann read a paper on "Researches on Methylbenzimidazole," which was a report on some of the author's work done under the direction of Prof. Zincke, at Marburg.

By special request Dr. Evans gave an extended résumé of the contents of his paper on "Ricinine" read by title at the December meeting.

FRANK I. SHEPHERD, *Secretary*.

#### NORTH EASTERN SECTION.

The regular monthly meeting of the section was held on Thursday evening, January 18th, President Little calling the meeting to order, with 63 members present.

After the transaction of business, Mr. Henry Howard presented a paper on "The Manufacture of Aluminum Sulphate by the Bayer Process," sketching the history of the alumina industry and explaining the theory and practice of the new method of manufacture.

A paper on "The Canned Foods Industry" by Mr. W. L. Underwood followed, in which was given the development of the business since its foundation in 1819, the difficulties which have been met, and how they have been overcome. In connection with this subject Mr. S. C. Prescott presented a paper on "The Preservation of Foods." This paper was illustrated by drawings and photographs of the micro-organisms which are found on, and in vegetables and other foods, and the author explained the methods by which these are destroyed. After examining the samples with which all the papers were illustrated, the meeting adjourned.

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The February meeting was held on Friday evening February 16th, at the Hotel Oxford, Vice-president Elihu Thomson in the chair and 60 members present.

The first paper of the evening was presented by Mr. Thomson on "The Properties of Carbon in Their Relation to Electrical Work." The author discussed the peculiar properties of carbon on which the development of applied electricity has so largely depended, calling special attention to those properties requisite for the terminals of arc lights, for incandescent light filaments, telephone transmitters and generating machine brushes.

The next paper was by Dr. F. H. Thorp on "The Potash Industry as seen at Stassfurt." After describing the position and composition of the different strata of the Stassfurt deposit, the author explained the method of mining and preparing for

market the different potash salts which are of commercial importance.

The section considered the resolutions which have been drawn up by the Committee on Instruments of Measure relating to the establishment of a National Standards Bureau, and on motion of Dr. H. P. Talbot the following resolution was adopted.

*Resolved*, That the members of the Northeastern Section of the American Chemical Society heartily endorse the proposed movement to secure the establishment of a National Standards Bureau for the verification of chemical apparatus, in connection with the United States Office of Weights and Measures; and that they desire to record as their opinion that such a bureau is urgently demanded in the interests of pure and applied chemistry in the United States.

At 10.10 the meeting adjourned.

W. H. WALKER, *Secretary*.

#### NORTH CAROLINA SECTION.

The fourth annual meeting of the North Carolina Section was called to order in the office of the State Chemist, Raleigh, at noon, February 24, 1900, by the presiding officer, Dr. Charles Baskerville. Sixteen members and invited guests were present.

After the reports of the different committees the following was introduced and carried :

*Resolved*, That it is the sense of the North Carolina Section that Article X, Sec. 1, of the Constitution of the American Chemical Society be so amended that when the local membership of a section is below 50 that section shall be entitled to draw annually an amount equivalent to one-third of the aggregate dues paid to the Society by its members. If the membership shall exceed 50 and be less than 200 the section shall be entitled to draw one-fourth; and if it shall reach a total of 200 the section shall be entitled to draw one-fifth.

A committee consisting of F. P. Venable, B. W. Kilgore, and W. A. Withers were appointed with carte-blanche to draft and forward resolutions to Congress in relation to the establishment and maintenance in connection with the Bureau of Weights and Measures, a department to graduate and verify weights and volumetric apparatus.

The following papers were read and discussed :

“Temperature for the Graduation of Volumetric Apparatus for Southern Laboratories,” by B. W. Kilgore; “On the Qual-

itative Determination of Tin; Arsenic and Antimony," by Charles Baskerville ; "Radio-active Bodies," by F. P. Venable; "Composition of Commercial Chromium Sulphate," by F. P. Venable; "Variable Ammonia Results in Mixed Fertilizers Containing Either Fish Scrap, Blood, Tankage, or Nitrate of Soda," by C. B. Williams ; "Chemical Economics," by Charles Baskerville.

Officers elected for the ensuing year are :

*President*, B. W. Kilgore ; *Vice-president*, W. J. Martin, Jr.; *Secretary and Treasurer*, C. B. Williams ; *Representative in Council for 1901*, Charles Baskerville ; *Executive Committee*, B. W. Kilgore, W. J. Martin, Jr., and C. B. Williams.

There being no further business the section adjourned.

C. B. WILLIAMS, *Secretary*.

#### PHILADELPHIA SECTION.

The seventh meeting was called to order in the Harrison Laboratory, University of Penna., January 18, 1900, at 8.20 P.M., 13 members being present. The presiding officer being absent Dr. Mathews was elected chairman for the evening. The minutes of the last meeting were read and approved.

The recommendation of the Finance Committee of the American Chemical Society, in relation to the distribution of dues for the benefit of the local sections, was read and discussed by Messrs. Shinn, Mathews, Kebler, and others. It was moved and seconded that the recommendation of the Finance Committee be accepted. Carried.

The following papers were presented :

"A Study in Iodination" by J. F. X. Harold, in which he called attention to the fact that it appeared that nobody had studied the reaction resulting from the action of hydrogen sulphide on iodine in the presence of alcohols, such as methyl alcohol, ethyl alcohol, etc. He showed that in the presence of an excess of iodine, the nascent hydriodic acid formed, attacked the alcohols forming iodides of the alcohol radical.

Lyman F. Kebler called attention to some of the exceedingly stringent requirements of the U. S. Pharmacopoeia, such as 100 per cent. purity, the absolute exclusion of chlorides and sulphates in such products as sodium benzoate, lithium carbonate, potassium hypophosphite, etc. He thought it very desirable to

have high standards, but they should not be beyond a point reasonably attainable. Many inconsistencies were pointed out in the 1890 edition. He also discussed at some length, why the American Chemical Society should be represented by several delegates at the Decennial Pharmacopoeial Convention. This may not be feasible for the convention that convenes next May, but in view of the fact that several of the states have already passed Food and Drug Adulteration Laws, making the U. S. P. standard in cases under these laws, it seems eminently desirable that the American Chemical Society should have representatives on the 1900 U. S. Pharmacopoeial Revision Committee.

The meeting adjourned at 9.45 P.M.

F. H. DODGE, *Secretary*.

#### COLUMBUS SECTION.

The Columbus Section has held its regular monthly meetings, the following papers having been presented during the present collegiate year.

“Reminiscences of Bunsen,” by S. A. Norton; “Cyclic Methylene Compounds,” by C. C. Howard; “A Discussion of Werner’s Hypothesis,” by Wm. E. Henderson; “The Action of  $\alpha$ -Acylphenylhydrazines on Chlorquinones,” by Wm. McPherson; “The Detection of Blood,” by A. M. Bleile; “The Midwinter Meeting of the American Chemical Society,” by Wm. McPherson.

The following officers have been elected for the year:

*President*, H. A. Weber; *Secretary*, Wm. McPherson; *Treasurer*, W. E. Henderson; *Committee on Membership*, G. B. Kauffman, A. M. Bleile; *Member of Council*, Wm. McPherson.

WILLIAM MCPHERSON, *Secretary*.

#### NEW YORK SECTION.

The regular meeting of the New York Section was held in the assembly room of the Chemists’ Club, 108 West 55th Street, on Friday evening, February 9th, at 8.30 P.M., Dr. C. F. McKenna presiding. There were about 50 members present.

Resolutions relative to a National Standards Bureau, forwarded by the chairman of the Committee on Standards of Instruments of Measure of the American Chemical Society, were read and, on motion, approved.

The following papers were then read : "The Technical Analysis of Rope and Twine," by Durand Woodman ; "A New Synthesis in the Phen-miazin Series," by M. T. Bogert and August Gotthelf ; "On the History of Photo-chemical Improvements, with Experiments," by Maximilian Toch.

A motion was made and seconded empowering the chair to appoint a committee to arrange for a meeting to be devoted to "Laboratory Apparatus and Products."

The meeting adjourned to meet March 9th.

DURAND WOODMAN, *Secretary*.



## Proceedings.

The twenty-first general meeting of the American Chemical Society will be held in New York City, Monday and Tuesday, June 25 and 26, 1900. Members desiring to present papers are urged to send titles and abstracts as soon as possible to the secretary, Albert C. Hale, 551 Putnam Ave., Brooklyn, N. Y.

### COUNCIL.

The amendments to the by-laws offered by Dr. Hillebrand were not adopted, a majority of the council voting against them.

#### NAMES PROPOSED FOR MEMBERSHIP.

Berkeley, Wm. N., San Juan, Puerto Rico.  
Bertelli, Riccardo, 20 W. 16th St., N. Y. City.  
Blake, Lucien I., Univ. of Kas., Lawrence, Kas.  
Colley, Bernard T., care C. K. C. S. & R. Co., Argentine, Kas.  
Davis, Charles B., 518 Manhattan Ave., N. Y. City.  
Ebaugh, W. Clarence., 3741 Lancaster Ave., Philadelphia, Pa.  
Ginder, W. H. H., Vandergrift, Pa.  
Hatchett, Roger H., Argentine, Kas.  
Hill, Edwin A., Patent Office, Washington, D. C.  
Hofmann, Ottokar, Argentine, Kas.  
Irwin, Edward B., 714 W. 11th St., Kansas City, Mo.  
Jessup, A. E., Office of Supervising Architect, Treasury Dept., Washington, D. C.  
Johnson, Flowmoy C., 714 Union St., New Orleans, La.  
Koelle, Carl, Argentine, Kas.  
Moechel, Jean Robert, 710 Wyandotte St., Kansas City, Mo.  
Neilson, Thomas, Tucson, Ariz.  
Neish, Arthur C., Columbia Univ., N. Y. City.  
Peters, Fredus N., Central High School, Kansas City, Mo.  
Rudinck, Paul F. A., 3701 S. Lincoln St., Chicago, Ill.  
Sloane, T. O. Coner, 39 Wall St., N. Y. City.  
Smither, F. W., 36 Cole Bldg., Nashville, Tenn.  
Torrey, Henry A., 75 S. Prospect St., Burlington, Vt.  
Whipple, Geo. C., Flatbush Ave. & Eastern Parkway, Brooklyn, N. Y.  
Whitten, W. H., Jr., Westport High School, Kansas City, Mo.  
Zeizler, John Clayton, Torpedo Station, Newport, R. I.

#### NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Harriman, Norman F., Ann Arbor, Mich.  
Wellard, H. H., 520 E. Ann St., Ann Arbor, Mich.

## NEW MEMBERS ELECTED MARCH 9, 1900.

Armsby, Prof. H. P., State College, Pa. .  
 Arnott, Geo. W. Campbell, 27 William St., N. Y. City.  
 Bach, August, 537 Nelson St., Chicago, Ill.  
 Bullard, Frank D., 245 Bradbury Block, Los Angeles, Cal.  
 Cuadrado, Gaston A., Calle de la Habana, 112, Habana, Cuba.  
 Douglas, William, Plantation Diamond, Demerara, British  
 Guiana.  
 Gardunio, Jesur, Aguascalientes, Mexico.  
 Goodell, Geo. A., 284 St. Nicholas Ave., N. Y. City.  
 Hamlin, Addison, 25 5th St., Bangor, Me.  
 Herger, Charles G., 11 Putnam St., Buffalo, N. Y.  
 Hulett, George A., 706 S. Thayer St., Ann Arbor, Mich.  
 Lihme, C. B., care of Ill. Zinc Co., Peru, Ill.  
 Mills, James E., Chapel Hill, N. C.  
 Mork, Harry S., 21 Wabeno St., Roxbury, Mass.  
 Norris, Robert S., Santa Maria, Cal.  
 Remington, Joseph P., 1832 Pine St., Philadelphia.  
 Richards, Joseph, 1802 Catherine St., Philadelphia.  
 Richardson, Wm. D., 4803 Madison Ave., Chicago, Ill.  
 Ross, Herbert W., 1070 16th St., Oakland, Cal.  
 Syme, W. A., Raleigh, N. C.  
 Thorne, Ernest E. H., Bridgetown, Barbadoes, B. W. I.  
 Thurlow, Nathaniel, 55 New St., Newark, N. J.  
 Weld, Fred C., Littleton, Mass.  
 Wolf, Ernst, 214 E. 82nd St., N. Y. City.  
 Wolfe, J. V., Jr., Rochester, Mich.

## ASSOCIATES ELECTED MARCH 9, 1900.

Bates, Hugh H., 502 E. 3rd St., Cincinnati, O.  
 Berghausen, Oscar, 644 Crown St., Walnut Hills, Cincinnati, O.  
 Block, Jesse A., Polytechnic Institute, Worcester, Mass.

## CHANGES OF ADDRESS.

Affelder, Oscar I., care Pittsburg Gas & Coke Co., Otto, Pa.  
 Best, Otto, 16 Mastic Terrace, Alameda, Cal.  
 Busby, Fred E., Mass. Inst. Tech., Boston, Mass.  
 Chamberlin, W. E., 127 Pearl St., N. Y. City.  
 Couch, Guy E., Hartwell, Hamilton Co., Ohio.  
 Dodge, F. E., care Barrett Mfg. Co., Tucker & Bermuda Sts.,  
 Frankford, Pa.  
 Hanks, A. Abbott, 531 California St., San Francisco, Cal.  
 Hartman, Wm. E., Kalamazoo Gas Co., Kalamazoo, Mich.  
 Hough, George J., 2235 Sheridan Rd., Evanston, Ill.  
 Jones, A. B., Lock Box 741, Pittsburg, Pa.  
 Kelley, J. H., 315 N. Vine St., Nashville, Tenn.

Lichtenstein, A. F., 67 Elmwood Ave., N. Adams, Mass.  
Martin, M. A., U. S. Mint, San Francisco, Cal.  
Parmelee, C. W., care N. Y. & Boston Dyewood Co., 55 Beekman St., N. Y. City.  
Richardson, Clifford, N. Y. Testing Lab., L. I. City, N. Y.  
Skinner, Hervey J., care Moro Phillips Chem. Co., Camden, N. J.  
Tucker, S. A., Havemeyer Hall, Columbia Univ., N. Y. City.  
Walker, P. H., care Ala. Consolidated C. & I. Co., Gadsden, Ala.  
Watkins, W. H., 87 Poplar St., Roslindale, Mass.

## MEETINGS OF THE SECTIONS.

### PHILADELPHIA SECTION.

The eighth meeting was called to order February 15th, at 8.25 P.M. in the Harrison Laboratory, University of Pennsylvania, February 15th, 20 members being present, the presiding officer was in the chair. The minutes of the last meeting were read and approved.

A letter from the chairman of the Committee on "A National Standardizing Bureau" of the American Chemical Society, was read; also a set of resolutions, which after some discussion were adopted as read.

A motion was made that the section meet promptly at 8 o'clock in the future. Seconded and carried.

Mr. George Auchy presented the paper of the evening: "Remarks on Some Methods of Determining Carbon in Steel." The paper was discussed by Messrs. Meeker, MacFarland, Sargent, Job, and Jayne.

There being no further business the meeting adjourned at 10 P.M.

F. E. DODGE, *Secretary*.

### ORGANIZATION OF MICHIGAN SECTION.

The first meeting of the Michigan Section of the American Chemical Society was held at the house of Professor Prescott in Ann Arbor, on Friday, February 28th, at four in the afternoon. Of the 42 members of the section in the State, 26 had promised to be present, but the heavy snow on that day blocked railroad traffic to such an extent that most of the members not resident in Ann Arbor who attempted to come, spent the day in trains.

stalled in snow-drifts. The meeting was called to order by Professor Prescott, with 16 members of the section present, and Dr. Wiley, of Washington, as an invited guest. Professor R. C. Kedzie of the Agricultural College was elected temporary chairman. Dr. Prescott gave a short statement of the movement he had started leading to the granting of a charter to the Michigan Section with territory covering the state of Michigan, and headquarters at the University of Michigan. Dr. Wiley was asked for remarks and responded with his congratulations on the formation of the new section, and an account of the methods of the Washington Section. The by-laws recommended by the Committee of Arrangements were adopted and the following officers elected for the year 1900 :

*Presiding Officer*, Professor A. B. Prescott, Ann Arbor; *Secretary and Treasurer*, Alfred H. White, Ann Arbor; *Member of Council*, Professor Paul C. Freer, Ann Arbor; *Elective Members of Executive Committee*, A. F. Shattuck, Chemist Solvay Process Co., Detroit; F. S. Kedzie, Professor, Agricultural College; J. V. Wolfe, Jr., Chemist Detroit Sugar Co., Rochester.

At the close of the business meeting, the members were entertained at dinner by Professor Prescott, and later listened to an illustrated lecture by Professor Freer on "Liquid Air." Many of the members also attended the sessions of the State Farmers' Institute on the following day when Dr. Wiley and others spoke on various questions pertaining to the beet-sugar industry.

ALFRED H. WHITE, *Secretary*.

#### CHICAGO SECTION.

Two meetings of the Chicago Section were held during February at the Union Restaurant, 111 Randolph St.

On the 8th, Mr. D. H. Trowbridge gave a very interesting paper on the "Manufacture and Chemistry of Beet Sugar."

On the 28th, Prof. W. O. Atwater, of Wesleyan University, who was the guest of the section gave an informal talk on the respiration calorimeter and its results.

F. B. DAINS, *Secretary*.

## Proceedings.

### BOARD OF DIRECTORS.

A meeting of the Board of Directors of the American Chemical Society was held at the Chemists' Club, 108 W. 55th St., New York City, March 21, 1900. There were present Messrs. McMurtrie, Hale, Hallock, Doremus, and Smith.

The meeting was called to order by President McMurtrie at 8:20 P.M. The minutes of the previous meeting were approved, as recorded in the secretary's book. Upon motion of Dr. Doremus the following schedule of prices for the Journal was adopted, and all previous schedules of prices inconsistent therewith were repealed.

For volumes of either 10 or 12 numbers:

	To members.	To non-members.
Current volume .....	\$5.00	\$6.00
"    numbers .....	0.50	0.60
Back volumes.....	3.00	6.00
"    numbers .....	0.30	0.60

For volumes of less than 10 numbers:

	To members.	To non-members.
Volumes .....	\$3.00	\$6.00

Numbers at proportionate rates. Discount to dealers, 15 per cent. on prices to non-members.

The librarian was directed to have prepared 1000 copies of a circular letter setting forth the above prices.

In order to economize space in the library, the librarian was authorized to prepare for binding any unbound material belonging to the library.

He was also authorized to exchange or sell, at his discretion, any duplicate material; and further, to publish in the advertising pages of the Journal a list of the numbers missing from the files in the library.

The treasurer was authorized to pay the note of the Society which falls due March 27.

The board then adjourned to meet in the same place, Friday, March 23, at 3 P.M.

An adjourned meeting of the Board of Directors of the American Chemical Society was held at the Chemists' Club, 108 W. 55th St., New York, March 23, 1900. There were present Messrs. McMurtrie, Hale, Hallock, Dudley, Doremus, and Smith.

The meeting was called to order by President McMurtrie at 8:40 P.M. The minutes of the meeting held March 21, were read and approved.

Upon motion of Dr. Doremus the schedule of prices for the Journal adopted at the last meeting was reconsidered and was amended so as to read as follows:

For volumes of either 10 or 12 numbers:

	To members.	To non-members.
Current volume.....	\$5.00	\$6.00
"    numbers.....	0.50	0.60
Back volumes.....	4.00	6.00
"    numbers .....	0.40	0.60

For volumes of less than 10 numbers:

	To members.	To non-members.
Volumes.....	\$4.00	\$6.00

Numbers at proportionate rates. Discount to dealers, 15 per cent. on prices to non-members.

It was voted that the librarian be requested to furnish to the Board of Directors a survey of the sets of the Journal now the property of the Society that the same may be scheduled for sale.

The following preamble and resolutions were unanimously adopted:

" WHEREAS, in a letter to the secretary of the Society, dated February 6, 1900, formal notice of the termination of the contract for printing the Journal of the Society was given by the Chemical Publishing Company, and

WHEREAS, the Chemical Publishing Company, in a letter to the secretary, dated February 20, 1900, proposed to continue for a period of 6 months, from May to October, inclusive, to publish the Journal in consideration of a bonus of ten dollars (\$10) a month above the price fixed by the contract,

*Be it Resolved*, that the Board of Directors, by and with the consent of the council, hereby accepts the notice of the termination of the contract, and agrees to pay to the said Chemical Publishing Company the bonus of ten dollars (\$10) per month above

the price fixed by the contract, in consideration of the temporary continuation, in accordance with all the terms of the said contract of the publication of the Journal from May to October 1900, inclusive.

The minutes of the meeting were read and approved. The board then adjourned.

### COUNCIL.

The following report and recommendations have been received from the Committee on Standards for Instruments of Measure, and have been approved by the council.

January 10, 1900.

*To the Council of the American Chemical Society.*

GENTLEMEN: We, the undersigned, members of the Committee on Standards for Instruments of Measure of the American Chemical Society, have considered the resolutions transmitted herewith and beg to ask your favorable consideration and action upon them, in accordance with the following motion passed by the Society at the recent New Haven meeting:

“Moved to refer the suggestions and resolutions of Mr. Ewell to the Committee on Standards for Instruments of Measure for consideration and report to the council which is requested to take action in the matter; and, further, that the Committee on Standards for Instruments of Measure be empowered to increase its number for the purpose of considering this subject.”

We recommend further, that these resolutions be printed with the signatures of the officers and councilors of the Society, and in sufficient number so that one thousand copies will be available for the use of this committee after copies have been transmitted by the secretary of the Society to the persons or bodies designated in the resolutions and to as many additional persons or bodies as your wisdom may suggest.

Your committee, named in the motion quoted above and as enlarged in accordance therewith, beg to so interpret that motion that the powers therein granted will be fully utilized, and the duties therein imposed will be duly executed, by each member of the committee constituting himself a sub-committee of one to place a copy of the resolutions in the hands of every person whose interest and efforts he believes will aid the movement; and by persuading him, by personal letters or by conversation when possible, to seek to impress the importance of our request upon as many as possible of the members of the two houses of Congress and of the appropriate committees thereof.

We also ask that the proper committees and officers of the Society be empowered and directed to honor bills for expenditures

for postage incurred in the execution of this plan by the ten members constituting this committee.

Respectfully,

E. E. EWELL, *Chairman*,  
G. E. BARTON,  
C. E. LINEBARGER,  
H. P. TALBOT,  
LOUIS A. FISCHER,  
F. W. CLARKE,  
C. B. DUDLEY,  
E. W. MORLEY,  
C. E. MUNROE,  
H. W. WILEY.

*Committee on Standards for Instruments of Measure of the American Chemical Society.*

**RESOLUTIONS RELATIVE TO A NATIONAL STANDARDS BUREAU.**

WHEREAS, in the conduct of exact chemical and physical investigations, the use of apparatus of guaranteed accuracy is a necessity which is recognized by all physicists and chemists; and

WHEREAS, in foreign countries, notably in Germany and England, such guarantee is furnished by standardizing bureaus under the control of their respective governments; and

WHEREAS, at present the U. S. Office of Standard Weights and Measures does not possess appliances necessary for the verification of as wide a range of apparatus in kind and form as seems essential, nor the working force requisite to comply with legitimate demands for the verification and stamping of chemical and physical apparatus, thus compelling the importation of foreign-made apparatus when such official certification is desired; and,

WHEREAS, this state of affairs is not only unsatisfactory to all chemists, but also works injustice to our manufacturers of thermometers, hydrometers, volumetric apparatus and other chemical measuring instruments who can not supply the proper certification with such apparatus; therefore be it

*Resolved*, that the congress of the United States be urged to establish a National Standards Bureau in connection with the U. S. Office of Standard Weights and Measures which shall provide adequate facilities for making such verification of chemical measuring apparatus and for stamping the same, as are provided by foreign governments for similar work.

*Resolved* further, that a copy of the foregoing be forwarded to the Secretary of the Treasury, under whose control the present office of Standard Weights and Measures comes; to the Super-



intendent of the U. S. Coast and Geodetic Survey; to the President of the U. S. Senate; to the Speaker of the U. S. House of Representatives; to the Chairman and members of the Committee on Coinage, Weights and Measures; and, to the presiding officers of the various sections of this Society and to the presiding officers of other scientific bodies likely to be interested, with a request for the cooperation of those organizations in our efforts to secure for the U. S. Office of Standard Weights and Measures ample facilities, in point of apparatus and working force, to enable that office to comply with the requests for the verification of measuring instruments that may be made by American scientific workers.

E. E. EWELL, *Chairman*,  
G. E. BARTON,  
C. E. LINEBARGER,  
H. P. TALBOT,  
LOUIS A. FISCHER,  
F. W. CLARKE,  
C. B. DUDLEY,  
E. W. MORLEY,  
C. E. MUNROE,  
H. W. WILEY.

*Committee on Standards for Instruments of Measure of the American Chemical Society.*

REFERENCES TO SOME RECENT LITERATURE ON THIS SUBJECT.

"Volumetric Apparatus." By G. E. Barton. *J. Am. Chem. Soc.*, 20, 731-739 (1898).

"On the Facilities for Standardizing Chemical Apparatus Afforded by Foreign Governments and Our Own." By Louis A. Fischer. *J. Am. Chem. Soc.*, 20, 912-927 (1898).

"A Brief History of the Movement for Increasing the Accuracy and for Improving the Construction of Chemical Measuring Instruments." By Ervin E. Ewell. *J. Am. Chem. Soc.*, 21, 527-550 (1899).

"Maasanalytische Studien." By Dr. Julius Wagner. (A Book Review.) By H. P. Talbot. *J. Am. Chem. Soc.*, 21, 551-555 (1899).

"On the Limits of Accuracy in Technical Analysis." By J. Grossman. *J. Soc. Chem. Ind.*, 18, 977-981 (1899).

"The Regulations of the Physikalisch-Technische Reichsanstalt Relative to Thermometers." Translated by C. E. Linebarger. *J. Am. Chem. Soc.*, 22, 121 (1900).

NAMES PROPOSED FOR MEMBERSHIP.

Ackerman, Franz W., 54 Livingston St., Brooklyn, N. Y.  
Ansbacher, Louis A., 4 Murray St., N. Y. City.  
Braun, F. W., 501-505 N. Main St., Los Angeles, Cal.

Emery, A. L., Palo Alto, Cal.  
 Frazee, F. H., 416 Concord Ave., Detroit, Mich.  
 Gibbon, R. Fitz, 77 John St., N. Y. City.  
 Hartley, Kenneth, Kansas City, Kansas.  
 Hartford, James, 100 William St., N. Y. City.  
 Hess, Henry W., 1829 Summit Ave., Toledo, O.  
 Hummel, John A., State Capitol, St. Paul, Minn.  
 Landis, Edward K., 4025 Spruce St., Philadelphia.  
 Neumeister, E. J., Alma Sugar Co., Alma, Mich.  
 Nikaido, Yasajuro, 2375 O St., Lincoln, Nebr.  
 Russell, Herman, 721 E. Ann St., Ann Arbor, Mich.  
 Schnierwind, F., Ph.D., United Coke and Gas Co., 36 Wall St., N. Y.  
 Soper, George A., 251 W. 93d St., N. Y. City.  
 Van Riper, George B., Rutherford, N. J.  
 Veitch, Alexander, Clifton, Ariz.

#### NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Eccles, David C., 191 Dean St., Brooklyn, N. Y.  
 Kiehn, John F., 3631 S. Winchester Ave., Chicago, Ill.  
 Stierlin, E., 1110 Queen City Ave., Cincinnati, O.

#### NEW MEMBERS ELECTED APRIL 28, 1900.

Berkeley, Wm. N., San Juan, Puerto Rico.  
 Bertelli, Riccardo, 20 W. 16th St., N. Y. City.  
 Blake, Lucien I., Univ. of Kansas, Lawrence, Kas.  
 Colley, Bernard T., C. K. C. S. & R. Co., Argentine, Kas.  
 Davis, Charles B., 518 Manhattan Ave., N. Y. City.  
 Ebaugh, W. Clarence, 3741 Lancaster Ave., Philadelphia.  
 Ginder, W. H. H., Vandergrift, Pa.  
 Hatchett, Roger H., Argentine, Kas.  
 Hill, Edwin A., Patent Office, Washington, D. C.  
 Hofmann, Ottokar, Argentine, Kas.  
 Irwin, Edward B., 714 W. 11th St., Kansas City, Mo.  
 Jessup, A. E., Office of Supervising Architect, Treasury Dept., Washington, D. C.  
 Koelle, Carl, Argentine, Kas.  
 Moechel, Jean R., Ph.D., 710 Wyandotte St., Kansas City, Mo.  
 Neilson, Thomas, Tucson, Ariz.  
 Neish, Arthur C., Columbia University, N. Y. City.  
 Peters, Fredus N., Central High School, Kansas City, Mo.  
 Rudinck, Paul F. A., 3701 S. Lincoln St., Chicago.  
 Sloane, T. O'Connor, 39 Wall St., N. Y. City.  
 Smither, F. W., 36 Cole Building, Nashville, Tenn.  
 Torrey, Henry A., 75 S. Prospect St., Burlington, Vt.

Whipple, George C., Flatbush Ave. and Eastern Parkway, Brooklyn, N. Y.

Whitten, W. H., Jr., Westport High School, Kansas City, Mo.

Ziegler, John C., U. S. Torpedo Station, Newport, R. I.

ASSOCIATES ELECTED APRIL 28, 1900.

Harriman, Norman F., Ann Arbor, Mich.

Willard, H. H., 520 E. Ann St., Ann Arbor, Mich.

CHANGES OF ADDRESS.

Belden, A. W., Birmingham Cement Co., Ensley, Ala.

Bloomfield, L. M., Valencia via Catacamas Olancho, Honduras, C. A., via New Orleans.

Cluff, Clarence B., 6608 Stewart Ave., Chicago, Ill.

Granja, Rafael, care The Palen Co., Kingston, N. Y.

Haslwanter, Charles, 904 Flushing Ave., Brooklyn, N. Y.

Hayes-Campbell, J., 514 E. 6th St., Newport, Ky.

Kenan, Wm. R., Jr., care Trader's Paper Co., Lockport, N. Y.

Kirchgasser, W. C., 74 and 76 Laight St., N. Y. City.

Loeser, R. M., care First Nat. Bank, El Paso, Texas.

Luschka, Otto, care Seamon Chemical Laboratory and Assay Office, El Paso, Texas.

Magruder, E. W., Dept. of Agr., Richmond, Va.

Nelson, E. K., 4526 Oakenwald Ave., Chicago, Ill.

Power, F. B., The Wellcome Research Laboratories, 6 King St., Snow Hill, E. C., England.

Smith, H. E., 29 31st Street, Milwaukee, Wis.

Thatcher, R. W., Agr. Expt. Sta., Lincoln, Nebr.

Thurnauer, Gustav, Aurora Metal Co., Aurora, Ill.

Wrampelmeier, T. J., 320 California St., San Francisco, Cal.

Yeaton, Arthur C., Westbrook Sem., Portland, Me.

Zimmele, H. B., 53 South Washington Square, New York City.

MEETINGS OF THE SECTIONS.

MICHIGAN SECTION.

The Michigan Section met on Friday evening, April 27, in the parlors of the Normandie Hotel, Detroit, with 57 members and visitors in attendance. Before the meeting there was an informal dinner at which 26 were present. The following papers were presented :

"Filtration of Drinking Water." By A. F. Shattuck.

"Theory of Hardening of Steel." By E. D. Campbell.

"Distillation of Amalgams and Purification of Mercury."  
By Geo. A. Hulett.

The paper announced by Charles C. Sherrard was, at his request, postponed till the next meeting.

ALFRED H. WHITE, *Secretary*.

#### NEW YORK SECTION.

The March meeting of the New York Section was held at the Chemists' Club, on Friday evening, March 9th, Dr. C. F. McKenna presiding.

The annual meeting of the Society at large, it was announced, would be held in New York in June in conjunction with the meeting of the Association for the Advancement of Science, and on motion it was voted that the Executive Committee be authorized to prepare for the reception of the American Chemical Society in June, and to add to their number as may be necessary.

The following papers were read :

"Normal Chlorine Map of Long Island." By Messrs. G. C. Whipple and D. T. Jackson.

"A New Industrial Process for the Separation of Oxygen, Nitrogen, and Carbon Dioxide from the Atmosphere at Extraordinarily Small Cost." By Prof. Raoul Pictet.

After a vote of thanks to Prof. Pictet the meeting adjourned.

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The April meeting of the New York Section of the American Chemical Society, was held on Friday evening, April 6th, at the Chemists' Club, 108 West Fifty-fifth Street. Dr. C. F. McKenna presided, and the following papers were read :

"A Method of Obtaining Nucleic Acid." By Dr. P. A. Levene.

"Analysis of a Saline Deposit from Southern Nevada." By Ralph W. Bailey.

"Notes on the Ferrocyanide Titration of Zinc." By Dr. E. H. Miller and E. J. Hall.

Special announcement was made of an extra meeting to be held on May 2d for the exhibition of novel forms of apparatus, products, etc., and that the meeting would be in the nature of a reception, to which the ladies and friends of the members would be invited. The Section on this occasion will be the guest of the Chemists' Club.

An invitation to attend the next meeting of the New York Section of the Society of Chemical Industry, on the occasion of the presentation of a paper on "Petroleum and its Products," by Dr. C. F. Newberry, signed by Dr. Parker, was then read, after which the meeting adjourned. , DURAND WOODMAN, *Secretary*.

#### CINCINNATI SECTION.

The 74th regular meeting of the Cincinnati Section was held in the Chemical Lecture Room, Hanna Hall, University of Cincinnati, on Thursday evening, February 15, 1900. Prof. R. M. Hughes occupied the chair. 32 members and visitors were present.

A communication from the Chairman of the Committee on Standards of Measure, of the American Chemical Society, was referred to a committee consisting of the president and secretary, with power to act.

The paper of the evening, "Expert Evidence," was presented by Dr. Alfred Springer.

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The 75th regular meeting of the Cincinnati Section was held on Thursday evening, March 15th, at the usual place of meeting in Hanna Hall. Dr. Evans presided, and 22 members and visitors were in attendance.

The Committee on a National Standards Bureau reported that it had adopted the resolutions read at the February meeting and had forwarded copies to the officials mentioned in the communication from Mr. E. E. Ewell.

Mr. Lucien Fogetti addressed the section on the subject, "Fractional Distillation in Vacuo, with a New Form of Receiver." The discussion which followed was quite generally participated in. Following this Mr. Fogetti gave a very interesting account of Dr. Squibb's plant and process for the manufacture of ether and absolute alcohol.

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The 76th regular meeting of the Cincinnati Section was held on Saturday evening, April 14th, in the Chemical Lecture Room in Hanna Hall, with Dr. Evans in the chair. Twenty-nine members and visitors were present.

Mr. Robert W. Hochstetter presented the paper of the evening, "Indigo." The methods now used in India for cultivating

the plant and preparing the crude indigo of commerce were described. The more important methods of making synthetic indigo were discussed briefly. Methods of analysis were touched upon, and the paper was concluded by an interesting account of the ways in which indigo is used in dyeing, calico printing, and as a pigment. The paper was well illustrated by specimens of natural and artificial indigo and its products and by materials dyed and printed.

FRANK I. SHEPHERD, *Secretary*.

#### WASHINGTON SECTION.

The 116th regular meeting was held Thursday, February 8, 1900.

The following program was presented :

"The Adulteration of the Arsenical Insecticides," by J. K. Haywood.

"Uncompounded Chemicals under the War Revenue Act (with exhibition of specimens)," by C. A. Crampton and D. Simmons.

"The Relation of the Chemical Society to the Municipality," by Wirt Tassin.

"The Genesis of Hardpan," by F. K. Cameron.

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The 117th regular meeting was held Thursday, March 8, 1900.

The program was devoted to a symposium on iron and steel, as follows :

Iron : The raw materials ; chemistry of iron-ore smelting ; cast iron ; properties of iron.

Steel : The raw materials ; converting methods ; the mill ; castings, forgings, and plates ; special steels.

The participants were Messrs. Dewey and Tassin.

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The regular meeting was held April 12, 1900.

The first paper was read by Mr. J. K. Haywood, and was entitled "The Analysis of the Arsenical Insecticides." The paper consisted of a comparative study of various methods proposed for the analysis of these preparations.

The second paper of the evening, which was presented by Dr. H. C. Bolton, and entitled "A Claim for Priority," was read by the Secretary.

"The Journal of the American Chemical Society for March, 1900, contains a paper by Joseph W. Richards and Norman S.

Powell, entitled "Substitutes for Hydrochloric Acid in Testing Carbonates;" the authors find that potassium acid sulphate, oxalic acid, citric acid, and tartaric acid can be used in testing carbonates, producing effervescence more or less actively, and they give a table of results. The authors make no reference to previous work on the same lines, and this prompts me to make the claim that about twenty years ago I anticipated all their observations and published the results in periodicals accessible to every one.

"Between 1877 and 1882 I published three memoirs under the title 'Application of Organic Acids to the Examination of Minerals,' in which I showed the action of these acids on 200 mineral species, including carbonates, sulphides, oxides, silicates, and many others. I pointed out the usefulness of citric acid as a substitute for hydrochloric acid in the laboratory and in the field, and showed that by means of it certain minerals could be readily distinguished.

"These papers were printed in whole or in part in the following journals: *Chemical News*, Vols. 35, 36, 43, and 47; *Annals N. Y. Acad. Sciences*, Vols. I and II; *Proceedings American Assoc. Adv. Science*, Vol. 47; *Reports Brit. Assoc. Adv. Science*, Vol. 50; *Mineralogical Mag.*, Vol. IV; *Ber. d. chem. Ges.*, Vol. XIII; and abstracts appeared in many other journals. Moreover the use of citric acid in testing minerals was adopted by teachers in more than one scientific school, the use of potassium acid sulphate having been known long before. Finally Nason's edition of Elderhorst's 'Manual of Qualitative Blowpipe Analysis' (1881) gives a whole chapter to my method.

"It is gratifying to note that the results obtained by Richards and Powell agree well with mine. Coincidences of independent thought often occur, but in publishing a research some acknowledgment of previous work is generally made; had the authors made even a slight examination of familiar literature they would have found that their field of study had been thoroughly traversed."

The third paper was read by Dr. Cameron and was entitled "The Estimation of the Carbonates and Bicarbonates of the Alkalies," by F. K. Cameron and L. J. Briggs.

The last paper was read by Dr. Cameron and was entitled "The Solubility of Calcium Sulphate in Solutions of Other Salts," by F. K. Cameron and F. D. Gardner.

Mr. Chestnut exhibited specimens of plants used by the Indians in California, to stupefy fish which they use for food.

An adjourned meeting was held at Hopkins Hall, Johns Hopkins University, Baltimore, Md., on April 21, 1900.

Dr. Remsen welcomed the Society and explained that the Chemical Department of the University is now undergoing repairs after damage by fire. He gave an interesting account of the work in progress under his direction in the university laboratory.

The first paper of the evening was read by Dr. Simon and was entitled "A Storage Vessel for Solid Carbon Dioxide." The author exhibited an improved vessel, which he had designed, and which is giving universal satisfaction in the transportation of such materials as solid carbon dioxide and liquid air. In connection with the vessel, he exhibited some solid carbon dioxide which had been placed in it the day before and showed that there had been very little loss.

Professor Morse read a paper on the preparation of permanganic acid, in which he discussed various methods and showed that the electrolytic method had been most satisfactory. He described, in detail, the apparatus used for carrying out this method.

Dr. Bolton presented a paper entitled "An Experimental Study of Radio-active Substances." The paper was illustrated with photographs taken with radium light.

The last paper of the evening was read by Dr. F. W. Clarke and was entitled "The Action of Ammonium Chloride on Certain Silicates," by F. W. Clarke and George Steiger.

"A brief outline of the method of decomposition of some zeolites, by heating with ammonium chloride in a sealed tube, was first given.

"It was shown by the experiments that two of the formulas, hitherto given, to scolecite, natrolite, and prehnite, must be abandoned.

"Scolecite and natrolite give almost identical ammonium compounds, calcium having been replaced in the one case and sodium in the other. They also show these two zeolites to be probably salts of orthotrisilicic acid.

"In the case of prehnite the results were quite different, two experiments giving only 0.17 per cent. in one case and 0.22 per cent. in the other of ammonium in the product formed by their treatment. This different action shows that prehnite can no longer be classed with the former two.

"In the case of pectolite the results were so irregular that definite conclusions could not be drawn from the facts at hand. Some figures were given and a formula suggested."

W. H. KRUG, *Secretary.*



## Proceedings.

### COUNCIL.

The following resolutions have been approved by council :

WHEREAS, the laws of the several states controlling food adulterations are largely ineffective because of the interference of interstate commerce laws, and can be made effective only through national legislation,

AND WHEREAS, by bills now pending in the congress of the United States and particularly by bills numbered H. R. 9677 and Senate 2426, it is proposed to establish in the United States Department of Agriculture a bureau of chemistry, the director of which shall, under the direction of the secretary of agriculture, be charged with the chemical investigation of the foods produced and consumed throughout the country.

*Therefore be it resolved* by the Council of the American Chemical Society that the congress of the United States be, and is hereby, urged to promptly enact into law the said bills, namely H. R. 9677, and Senate 2426, and provide adequate facilities for effective prosecution of the provisions of the said bills.

*Resolved*, further, that a copy of this resolution be forwarded to the president of the United States Senate ; to the speaker of the House of Representatives ; to the chairman of the Committees on Agriculture and on Commerce and Manufactures of the Senate of the United States ; to the chairman of the Committee on Interstate Commerce of the House of Representatives ; to the secretary of agriculture, who shall be charged with the enforcement of the provisions of said bills, and to the presiding officers of the various sections of the Society, urging their cooperation in the movement to secure the establishment of the bureau of chemistry, which shall be charged with the scientific and chemical work required in the enforcement of the provisions of the said bills.

# **NAMES PROPOSED FOR MEMBERSHIP.**

Allen, Richard F., Hart Park, West New Brighton, Staten Id., N. Y.

Berolzheimer, Daniel D., 175 E. 79th St., N. Y. City.

Hancock, Wm. J., Erasmus Hall, High School, Brooklyn, N. Y.

Logan, Lily, Howardsville, Va.

Lohmann, Herman J., 90 Monticello Ave., Jersey City, N. J.

Norton, Mrs. Alice P., 47 Hancock St., Auburndale, Mass.

Richards, Alfred N., 437 W. 59th St., N. Y. City.

Stockwell, C. F., Bassett, Nebr.

Sundstrom, Carl, care Solvay Process Co., Detroit, Mich.

Sundstrom, Karl J., Trenton, Wayne Co., Mich.

Taylor, Thomas M., Oberlin, Ohio.

Torrey, Joseph, Jr., 8 Avon St., Cambridge, Mass.

Waddell, John, School of Mines, Kingston, Ont.

## **NAME PROPOSED FOR ASSOCIATE MEMBERSHIP.**

Pretzfeld, Charles J., 1211 Madison Ave., N. Y. City.

## **NEW MEMBERS ELECTED JUNE 12, 1900.**

Ackerman, Franz W., 54 Livingston St., Brooklyn, N. Y.

Ansbacher, Louis A., 4 Murray St., N. Y. City.

Emery, A. L., Palo Alto, Cal.

Fraze, F. H., 416 Concord Ave., Detroit, Mich.

Hartford, James, 100 William St., N. Y. City.

Hartley, Kenneth, Kansas City, Kans.

Hess, Henry W., 1829 Summit Ave., Toledo, O.

Hummel, John A., State Capitol, St. Paul, Minn.

Landis, Edward K., 4025 Spruce St., Philadelphia.

Mather, Henry A., care Verde Queen Copper Co., Jerome, Ariz.

Neumeister, E. J., Alma Sugar Co., Alma, Mich.

Nikaido, Yasajuro, 2375 O St., Lincoln, Nebr.

Russell, Herman, 721 E. Ann St., Ann Arbor, Mich.

Schnierwind, F., United Coke and Gas Co., 36 Wall St., N. Y. City.

Soper, George A., 251 W. 93rd St., N. Y. City.

Van Riper, George B., Rutherford, N. J.

## **ASSOCIATES ELECTED JUNE 12, 1900.**

Eccles, David C., 191 Dean St., Brooklyn, N. Y.

Kiehn, John F., 3631 S. Winchester Ave., Chicago, Ill.

Stierlin, E., 1110 Queen City Ave., Cincinnati, O.

## CHANGES OF ADDRESS.

- Ashley, Harrison E., 947 Acushnet Ave., New Bedford, Mass.  
 Bevier, Miss Isabel, Plymouth, Ohio.  
 Brewer, Chas. E., Wake Forest, N. C.  
 Clark, Clara, 201 N. Jackson St., Butte, Mont.  
 Dailey, J. Glanding, 327 Wharton St., Philadelphia, Pa.  
 Fosdick, E. H., 1505 S. Grand Ave., Los Angeles, Cal.  
 Jackson, Daniel D., 179 Sixth Ave., Brooklyn, N. Y.  
 Johnson, Treat B., 57 Otis St., E. Cambridge, Boston, Mass.  
 Labonde, Dr. Leon, 3601 S. Hower St., Los Angeles, Cal.  
 McIlhiney, P. C., 145 E. 23d St., N. Y. City.  
 Perkins, T. S., care California Tartar Co., 318 Front St., San Francisco, Cal.  
 Phalen, Wm. C., 13 Sadler St., Gloucester, Mass.  
 Phillips, Wm. D., 128 Pearl St., N. Y. City.  
 Richardson, Clifford, care N. Y. Testing Lab., Long Island City, N. Y.  
 Schüpphaus, Robert C., 174 Broadway, N. Y. City.  
 Skinner, Hewey J., care General Chem. Co., Moro Phillips Works, Camden, N. J.  
 Tuschka, Otto, care Seamon Lab., El Paso, Texas.  
 Willard, H. H., Union City, Mich.  
 Willey, Ogden G., Box 179, Berwyn, Ill.

## MEETINGS OF THE SECTIONS.

## CHICAGO SECTION.

The 34th regular meeting of the Chicago Section was held at the Union Restaurant, May 11, 1900.

Prof. W. A. Noyes, of the Rose Polytechnic Institute, gave a paper on the constitution of camphor, showing how the problem had been attacked and the evidence for the formula now assigned.

Dr. J. H. Long was elected member of the council from the Chicago Section.

F. B. DAINS, *Secretary*.

## NEW YORK SECTION.

The May meeting was held on the 12th, at the Chemists' Club, as usual, Dr. C. F. McKenna presiding. The following papers were read:

C. W. Volney: "New Extraction Apparatus."

C. W. Volney: "Artificial Musk."

P. A. Levene: "Modern Researches on the Chemistry of the Proteid Molecule."

J. A. Mathews: "Cobalticyanides of Bismuth."

Dr. Volney's artificial musk was exhibited and caused considerable discussion. It is said to be a compound belonging to the paraffin series, and therefore is a distinct departure from the idea that an artificial perfume must contain the "benzol ring." No analysis was given nor particulars of the method of preparation, these being reserved for a future communication. Asked whether his musk is composed of a saturated or unsaturated paraffin compound, Dr. Volney said that it is saturated. Dr. Schweitzer said that so far as he knew, it had never been claimed that an aromatic group was necessary in the synthetic musks. Dr. Stearns claims that nitrated bodies do not smell of true musk. Different persons, he said, are differently affected by the true musk odor, and many are incapable of deciding that an imitation is a good representative of the true flavor. In this way many substances were called artificial musk which would not pass even an arbitrary set of tests. It is not yet known what the essential element of true musk is, or whether it is preexistent, or is formed by a slow chemical change in the constituents of musk material. Baur has examined musk to determine whether nitrated bodies were present, but found none.

Dr. Levene's paper was an interesting review of the work which has been done and the views which have been held during the past two years on the chemistry of the protein compounds and the classifications of their constituents. In regard to the sulphur in their composition, he said it evidently existed in two forms or conditions of combination, one molecule being separable as hydrogen sulphide, the other remaining.

Dr. J. A. Mathews described an investigation of the cobalticyanides of bismuth designed to develop a process for separation of bismuth in analytical work—for instance, in the analysis of pig and refined lead. The conditions under which such an analysis is carried out were found, however, to prevent the complete precipitation of bismuth as cobalticyanide, and as yet he had not been able to make the practical application of the study of these salts which had been hoped for.

The meeting was addressed by Prof. Rising, of California, who said that much interest was manifested by the chemists of the Pacific coast in becoming members of the American Chemical

Society, and an application for a charter would soon be made.

Dr. McMurtrie, president of the Society, was present, and, invited to take the chair, said that in view of the approaching general meeting it was necessary that each member should bring out whatever subject he had in readiness for publication in time to have its title announced on the program. All such titles should be transmitted to the general secretary, A. C. Hale, 551 Putnam Ave., Brooklyn, N. Y., as early as practicable, to facilitate the preparation of the program and to enable the committee to arrange sufficient time for the sessions. Dr. Doremus announced the full list of sections, and ground covered thereby, in the congress of chemists to be held at Paris in July—also that titles of papers to be presented there should be forwarded not later than June 1.

The chairman referred to the special exhibition-reception meeting held on the 2nd inst. in the Assembly Room of the club, and suggested a vote of thanks to those who had assisted in making it a success. On motion, a vote of thanks was seconded and carried unanimously: to Dr. Elwyn Waller for the handsome roses sent from his greenhouses to decorate the tables; to the firms who made special exhibits of apparatus, minerals, and chemical products; and to Dr. E. E. Smith and his committee for their arduous labor in arranging the details of catalogue, printing, etc.

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The June meeting of the New York Section of the American Chemical Society was held on the 8th inst. at the Chemists' Club. The retiring chairman, Dr. Chas. F. McKenna, invited the president of the Society, Dr. William McMurtrie, to preside. An address was made by Dr. McKenna on the "Advancement in the Study of the Properties of the Metals," and on the "Present and Future of the New York Section of the American Chemical Society."

The election of officers for the ensuing year resulted as follows: *Chairman*, Dr. C. A. Doremus; *Secretary and Treasurer*, Durand Woodman; *Executive Committee*, C. F. McKenna, M. T. Bogert, and P. C. McIlhiney.

The following papers were then read:

"Comparison of Iodine and Bromine Figures of Various Fatty Oils," by H. T. Vulté and Lily Logan.

"The Chemistry of Materials used in Perfumery and Kindred Arts," by T. C. Stearns.

"Rapid Method for Separation of Cadmium, Bismuth, etc., from Zinc and Manganese," by Geo. C. Stone.

"On the Oxidation of Platinum," by Dr. R. C. Hall.

A motion was made and seconded that a fund should be raised for a prize for the best paper read before the Society during each season. This was in pursuance of a suggestion made by the chairman in his address.

Notice was given of the general meeting of the American Chemical Society, to be held in the latter part of the month, after which the Section adjourned.

DURAND WOODMAN, *Secretary*.

## Proceedings.

### COUNCIL.

The following resolution was approved by Council, June 15, 1900:

*Resolved*, That the President of the American Chemical Society is hereby authorized and directed to appoint a committee, of which he himself shall be Chairman, with power to confer and to make arrangements with Section C, with any officers or committees of the American Association for the Advancement of Science, and with other organizations affiliated with the American Association for the Advancement of Science, for future summer meetings of the American Chemical Society and Section C."

#### NAMES PROPOSED FOR MEMBERSHIP.

Bolling, Randolph, Va. I. C. & C. Co., Radford Blast Furnace, Radford, Va.

Brown, Walter B., care Nelson Morris & Co., U. S. Yards, Chicago, Ill.

Cabot, Samuel, 70 Kilby St., Boston, Mass.

Diehl, Oscar C., care Parke, Davis & Co., Detroit, Mich.

Hall, Everett J., Passaic, N. J.

Hillyer, Homer W., Madison, Wis.

Kniffen, Frederick, Indian Head, Md.

Lucas, Alfred, Survey Dept., Public Works Ministry, Cairo, Egypt.

Lyons, Philip D., Md. Steel Co., Sparrows Point, Md.

Nathan, Albert F., 603 Mumford Court, Kansas City, Mo.

Reid, E. Emmet, College of Charleston, Charleston, S. C.

Root, W. W., 186 Eugenie St., Chicago, Ill.

Sears, Frederick E., St. Paul's School, Concord, N. H.

Seward, George O., Holcomb Rock, Va.

Walker, Claude F., Calumet, Mich.  
Wiley, Walter B., Bramwell, W. Va.  
Willcox, Frank A., Oakland, Bergen Co., N. J.

**NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.**

Calvert, Joseph E., Etna, Allegheny Co., Pa.  
Condit, Louis C., 139 Lafayette Ave., Brooklyn, N. Y.  
Kohnstamm, Lothair S., 133 E. 71st St., New York City.  
Thomas, T. Lewis, 71 Broadway, New York City.  
Warren, Robert, S. 6th St., Terre Haute, Ind.

**CHANGES OF ADDRESS.**

Archibald, Eben H., Harmony, Colchester Co., Nova Scotia.  
Arnold, Fred. N., care The N. K. Fairbank Co., St. Louis, Mo.  
Arnott, G. W. Campbell, 26 Broadway, New York City.  
Beach, W. M., 954 W. North Ave., Allegheny, Pa.  
Behr, Gustave E., Jr., Harvard Univ., Cambridge, Mass.  
Bevier, Miss Isabel, Univ. of Ill., Champaign, Ill.  
Browne, Charles A., Jr., Univ. of Goettingen, Goettingen, Germany.  
Burk, W. E., Male High School, Louisville, Ky.  
Burn, Harry, care Sloss-Sheffield S. & I. Co., Birmingham, Ala.  
Campbell, Archibald, 3140 Duwell Ave., Walnut Hills, Cincinnati, Ohio.  
Campbell, George F., 82 Broadway, New Haven, Conn.  
Cayvan, L. L., 499 Adams St., Chicago, Ill.  
Coutie, William, 2129 7th Ave., Troy, N. Y.  
Craig, A. G., 6112 Station St., Pittsburg, Pa.  
Davis, Charles B., care Dr. Wyatt, 39 S. William St., New York City.  
Davison, John M., 340 Oxford St., Rochester, N. Y.  
Dorr, John V. N., Golden Gate M. & M. Co., Deadwood, S. D.  
Downey, James E., High School, Holyoke, Mass.  
Dustin, Guy K., 30 Lenango St., Binghamton, N. Y.  
Ellis, Carleton, 195 Winchester St., Keene, N. H.  
Ellis, Geo. H., 163 Randolph St., Chicago, Ill.  
Fischer, Robert, 810 Franklin Ave., Columbus, O.  
Gallivan, F. B., 56 Prospect Place, Brooklyn, N. Y.  
Garrigues, W. E., 1123 Broadway, New York City.  
Given, Arthur, 1 Plymton St., Worcester, Mass.  
Hall, Robert W., University Heights, Bronx, N. Y. City.  
Hamilton, Louis P., 222 E. Beaux St., Washington, Pa.  
Hodges, G. C., Box 88, New Hartford, N. Y.



Horsford, Roger F., care Am. Bell Telephone Co., 125 Milk St.  
Boston, Mass

Isaacs, A. S., 1214 Sheffield St., Allegheny, Pa.

Keller, A. C., Apartado A., Aguascalientes, Mexico.

Kittredge, Harvey G., The Kay and Ess. Co., Dayton, O.

Krug, W. H., Div. of Chem., U. S. Dept. of Agr., Washington,  
D. C.

Levine, Edmund J., 337 W. 88th St., New York City.

Lippincott, Warren B., Am. S. & R. Co., Argentine, Kas.

Lythgoe, H. C., Room 501, State House, Boston, Mass.

Mabery, C. F., North Gorham, Me.

Mathewson, E. P., Establacimiente del Playa Blanca, Antofogasta, Chili, S. C.

Mixer, C. T., Joplin, Mo.

Murrill, Paul, Hickory, N. C.

Parker, T. J., care General Chem. Co., 32 Liberty St., New  
York City.

Parmelee, H. C., 1733 High St., Denver Colo.

Porter John J., Observatory Ave., Hyde Park, Cleveland, O.

Redding, Allen C., Golconda Mine, Sumpter, Ore.

Reese, H. J., Livingston, Mont.

Richardson, Clifford, Director N. Y. Testing Lab., Long Is-  
land City, N. Y.

Rickards, Burt R., 162 Salem St., Malden, Mass.

Ritchey, Joseph C., Nat. Steel Co., Mingo Junction, O.

Rosell, Claude A. O., 268 W. Broadway, New York City.

Sanborn, E. R., care Alice Furnace, Sharpsville, Pa.

Smith, A. L., 653 Union Ave., Englewood, Ill.

Soper, G. A., 29 Broadway, New York City.

Sticht, Gustave A. H., care Tartar Chem. Co., Jersey City,  
N. J.

Stone, Geo. C., 115 Broadway, New York City.

Syme, Wm. A., cor. North and Person Sts., Raleigh, N. C.

Thomas, N. Wiley, Rooms 330-332, City Hall, Philadelphia,  
Pa.

Torrey, Henry A., 75 S. Prospect St., Burlington, Vt.

Touceda, Enrique, Room 44, 51 State St., Albany, N. Y.

Wilder, S. W., Jr., 77 Broad St., Boston, Mass.

Worstall, R. A., 1246 E. Madison Ave., Cleveland, O.

#### ADDRESS WANTED.

Stursberg, J. A., formerly of 18 E. 67th St., N. Y. City.

## MEETINGS OF THE SECTIONS.

### WASHINGTON SECTION.

The regular meeting was held May 10th.

Mr. Edwin A. Hill presented a paper entitled "On a System of Chemical Indexing Adopted by the Classification Division of the U. S. Patent Office."

WILLIAM H. KRUG, *Secretary.*

Issued with August Number, 1900.

## Proceedings.

### TWENTY-FIRST GENERAL MEETING.

The Twenty-first General Meeting of the American Chemical Society was called to order at 12.35 P.M., Monday, June 25, 1900, in Room 309, Havemeyer Hall, Columbia University, New York City.

The president introduced Dr. Charles F. McKenna, chairman of the New York Section, who addressed a few words of welcome to the visiting chemists.

Responses were made by Prof. Jas. Lewis Howe, on behalf of Section C of the American Association for the Advancement of Science, and Dr. Wm. McMurtrie, on behalf of the American Chemical Society.

After a few announcements, the meeting was adjourned till 2 P.M.

*Afternoon Session.*—At 2 P.M. the Society was called to order again and the minutes of the last general meeting as already printed in the Journal were approved.

A paper on "The Composition of Abietic Acid" was read in abstract by the author, Hermann A. Loos.

Mr. Marston Taylor Bogert read a paper on "Experiments with Some Substituted Benzoic Acids and their Nitriles," prepared by himself and August H. Gotthelf. This was followed by two other papers by the same authors, the titles of the papers being "The Direct Synthesis of Ketodihydroquinazolines from Orthoamido Nitriles" and "The Direct Synthesis of Ketodihydroquinazolines from Orthoamido Acids."

A paper "On Some Derivatives of Phenyl Ether," by H. W.

Hillyer, was read by the author, after which the session adjourned.

A meeting of the Council of the Society was held in Room 311, Havemeyer Hall, at 4.15 P.M. At 8 P.M. the chemists enjoyed a "Smoker" at the Chemists' Club, 108 W. 55th St., given by the New York Section of the Society.

TUESDAY, JUNE 26, 1900.

*Forenoon Session.*—The morning session was called to order at 10.40 A.M. in the Assembly Hall of the Chemists' Club. Mr. T. J. Parker, vice-president of the Club, was introduced by the president, and welcomed the chemists in a few words.

A paper on "The Metric System, Past, Present, and Prospective," was presented by Rufus P. Williams, and discussed by Messrs. Parker, Seaman, and Hillebrand, the last of whom offered the following resolution :

*Resolved*, That this Society is strongly in favor of the passage of H. R. Bill 104, looking to the adoption and use of the Metric System, and that the secretary be instructed to so inform the Chairman of the Committee on Coinage, Weights, and Measures of the House of Representatives in Washington.

This was referred without debate to the Council for consideration and report at the December meeting as to the advisability of the Society adopting it.

A paper on "The Reduction Products of Dehydromucic Acid" was read by A. S. Wheeler and discussed by W. A. Noyes. The following papers were then presented by their authors :

"The Detection of Coal-tar Dyes in Food Products," by A. L. Winton.

"Estimation of Fat in Sweetened Condensed Milk," by Joseph F. Geisler.

"Some Analyses of Milk and Cream, with Reference to the Condition of Fat Globules," by H. C. Sherman.

"The Action of Various Preservatives upon Cider," by E. H. S. Bailey.

"The Determination of the Formulas of the Hydrocarbons and Chlorine Derivatives in Pennsylvania, California, Japanese

and Canadian Petroleum by Molecular Refraction," by Charles F. Mabery and O. J. Sieplein.

"The Sulphur Compounds and their Oxidation Products and the Unsaturated Hydrocarbons in Canadian Petroleum," by Charles F. Mabery and W. O. Quayle.

"Composition of the Hydrocarbons in Pennsylvania Petroleum, Liquids and Solids above 216°," by Charles F. Mabery.

"Composition of the Hydrocarbons in California Petroleum, Liquids and Solids," by Charles F. Mabery.

"Composition of the Nitrogen Compounds in California Petroleum," by Charles F. Mabery.

"The Chlorine Derivatives of the Hydrocarbons in California Petroleum," by Charles F. Mabery and O. J. Sieplein.

The meeting was then adjourned till 2.30 P.M.

*Afternoon Session.*—The afternoon session was called to order at 2.30 P.M. at the Chemists' Club.

The secretary called attention to the death of Mrs. Rachel Lloyd, a former member of the Society, and moved that Dr. C. F. Mabery be requested to prepare a suitable memorial to be printed in the Journal. The motion was passed unanimously.

The committee appointed to prepare a memorial on the late Professor Bunsen presented its report by title. The report was referred to the Committee on Papers and Publications.

After some announcements the following papers were read :

"Experimental Demonstration of the Manufacture of Sulphuric Acid" (by the Contact Process), by Charles L. Reese and G. C. Stone.

"Production of Caustic Soda and Bleaching-powder by Electrolysis," by Hugh K. Moore.

"The Incubator Test for Determining the Purity of Sewage Effluents," by Leonard P. Kinnicutt.

"Bacterial Action in the Purification of Sewage by Chemicals," by Leonard P. Kinnicutt.

"An Experimental Study of the Gas-producing Power of *Bacillus Coli Communis* under Different Conditions of Environment," by Mary Engle Pennington and G. C. Küsel. This paper was read by Dr. Pennington and discussed by Messrs. Harper and Doremus.

The secretary moved that Professor Edward W. Morley, of Cleveland, Ohio, and Professor Wilhelm Ostwald, of Leipzig, Germany, be elected honorary members of the Society. The motion was adopted unanimously.

After the reading of a "Note on the Landsberger-McCoy Apparatus," by W. D. Bancroft, and a paper on "The Action of Potassium Hydroxide on Chloroform," by A. P. Saunders, read by Prof. Bancroft, and some announcements, the Twenty-first General Meeting of the Society was adjourned *sine die*.

#### WEDNESDAY.

At 7 P.M. on Wednesday, June 27, the chemists enjoyed a dinner at Hotel Majestic. On account of the unpromising weather the dinner was in the dining hall of the hotel, instead of being upon the roof garden as had been contemplated.

Dr. Charles F. McKenna presided and acted as toast-master.

Toasts were responded to by President William McMurtrie, Prof. L. O. Howard, permanent secretary of the A.A.A.S., Prof. Jas. Lewis Howe, vice-president A. A. A. S., Section C, Dr. Mary Engle Pennington, Prof. Elihu Thomson, Dr. Charles Baskerville, Prof. B. W. Kilgore, and Dr. L. P. Kinnicutt.

ALBERT C. HALE, *Secretary*.

#### BOARD OF DIRECTORS.

The Board of Directors of the American Chemical Society met at the Chemists' Club, New York City, at 9.45 P.M., June 25, 1900. There were present Messrs. McMurtrie, Hale, Hallock, Doremus, and Smith.

The sum of fifty dollars, or so much thereof as may be necessary, was appropriated from funds of the Society not otherwise appropriated for the purpose of preparing a card catalogue for the library.

The librarian was authorized to expend a sum not exceeding twenty-five dollars for new shelving for the library.

The sum of fifteen dollars and fifty-five cents was appropriated to reimburse the expenses of the president in going to Washington to appear before the Committee of Congress upon the question of establishing a National Standards Bureau.

The president of the Society was authorized to take from the library temporarily such material as he may wish to use in preparing a review of the progress of industrial chemistry.

It was ordered that the insurance on the library be kept sufficient to cover the current stock of Journals on hand from time to time.

The Board then adjourned.

ALBERT C. HALE, *Secretary*.

### COUNCIL.

A meeting of the Council of the American Chemical Society was held in Room 311, Havemeyer Hall, Columbia University, New York City, at 4.15 P.M., Monday, June 25, 1900.

There were present Messrs. McMurtrie, Catlin, Doremus, Hale, Hallock, Hart, Hillebrand, Kinnicutt, Long, Mabery, Mathews, McPherson, Munroe, A. A. Noyes, W. A. Noyes, E. E. Smith, and Venable.

The minutes of the December meeting, as already printed in the Journal, were approved.

The president gave a brief review of the present condition and needs of the Society, after which the following resolution was adopted :

*Resolved*, That Sections (1) and (2) of the Finance Committee's report as adopted at the last general meeting of the Society be amended to read as follows : 81E

- (1) Before December 15 of each year, each officer of the Society shall submit to the president a schedule comprising the estimated expenses of his office, in detail, for the ensuing year. The president shall, in advance of the annual meeting, submit these estimates to a Committee on Estimates, consisting of the Finance Committee, the president, the secretary, and the treasurer, who shall consider them in the relation to the probable income of the Society for the ensuing year, and report the result of their deliberations, together with the original estimates, with recommendations of appropriations to the Council at the annual meeting.
- (2) After such report shall have been submitted, the Council shall recommend such appropriations for

each office as may be deemed advisable, and the Directors shall, upon such recommendation from the Council, make necessary appropriations in accordance therewith.

After some discussion regarding the question of apportionment of the funds of the Society for the benefit of Local Sections, the following motion, presented by W. A. Noyes, was adopted:

*Resolved*, That the Council recommends that the Local Sections be requested to keep their expenses as low as they deem consistent with the best interests of the Society in their locality; also that they be requested not to draw funds from the treasury except as required for the payment of bills.

On motion of Dr. Mabery, this motion was reconsidered, and, after some discussion, again passed by the Council.

The following resolutions were also passed :

*Resolved*, That the president of the Society be authorized and directed to appoint a committee, of which he himself shall be chairman, with power to arrange for the celebration of the twenty-fifth anniversary of the foundation of the Society, which will occur on April 6, 1901, in conformity with the action taken by the Council upon that subject at the last general meeting of the Society.

*Resolved*, That the president of the Society appoint a committee of five, of which he himself shall be one, with power to make a new contract for the printing of the Journal of the Society.

The following named gentlemen were appointed to constitute the Committee on Contract : Messrs. McMurtrie, C. B. Dudley, M. L. Griffin, A. D. Little, and H. N. Stokes.

The following communication from the librarian was read by the secretary and ordered to be included in the minutes of the Council, and printed in the Journal :

NEW YORK, June 23, 1900.

*Dr. Wm. McMurtrie, President American Chemical Society :*

DEAR SIR : I submit the following statement in response to a resolution of the Board of Directors of the Society "that the librarian be requested to furnish to the Board of Directors a survey of the sets of the Journal now the property of the Society that the same may be scheduled for use."



There have been 10 issues of the Proceedings and 216 issues of the Journal.

There are at present in the custody of the librarian 3,672 copies of the Proceedings, and 44,756 copies of the Journal, or a total of 48,428 copies. These are stored as follows :

Proceedings in Garfield Storage .....	3,213	
"            at Chemists' Club.....	459	
	<hr/>	3,672
Journals in Garfield Storage .....	33,257	
"            at Chemists' Club .....	11,499	
	<hr/>	44,756
Total Proceedings and Journals...		48,428

These figures so far as they refer to the material in the Garfield Storage Warehouse are based on an inventory furnished me by a former librarian.

Of the Proceedings, No. 5 of Vol. II is out of print, but of the other issues the number of copies ranges from 100 in the case of Vol. I, No. 1, to 672 in that of Vol. II, No. 2.

The issues of the Journal of which we have less than 50 copies each are as follows :

	Copies.
Vol. III, single number 1-6.....	38
"    "    number 7.....	35
"    "    single number 8-12 .....	25
"    IV, number 12 .....	48
"    V, single number 2-3.....	48
"    VI, "    "    1-2.....	26
"    "    number 3.....	18
"    "    "    4 .....	30
"    XVII, number 10 .....	34
"    XVIII, "    6 .....	43
"    XX, "    3 ....	42

Or there are 11 issues of which we have less than 50 copies each. In addition to these there are :

31 issues of which we have from 50 to 100 copies each.									
132	"	"	"	"	"	"	100 to 250	"	"
24	"	"	"	"	"	"	250 to 500	"	"
18	"	"	"	"	"	"	over 500 copies each.		

It appears, therefore, that at the present time we can not furnish a set of the Proceedings, and can furnish only eighteen sets

of the Journal. In view of this fact, I would suggest that at least ten sets of the Journal be reserved to be sold only in sets.

It will be noticed from the foregoing statement that nearly one-fourth of our entire stock of Proceedings and Journals is stored at the Chemists' Club in 55th St. The library is covered by insurance, but so far as I know the stock of Journals is not. I would suggest that a special policy be taken out, the amount of which shall be increased monthly or bimonthly by a sum sufficient to cover the issues received in the meantime, less those disposed of.

The stock of Journals stored at the Chemists' Club is deposited in a room which the librarians of the Society have simply appropriated without any action on the part of the Trustees of the club granting the use of such room. The club may at any time require this space, in which event it would be necessary for the librarian to find other storage for these Journals. I would therefore recommend that the Council be requested to take such action as may be necessary either to rent from the club the room at present used by the Society, or to procure storage elsewhere. The space available in this room will probably answer our requirements for two or three years, at the end of which time our supply of certain issues will doubtless be so much reduced as to make it necessary for the Society to determine whether the present policy of carrying a stock of each issue, with the necessity of reissuing certain numbers from time to time, be continued, or whether it may not be advisable to abandon the present plan, and to supply the Journals only so long as the first issue lasts.

Yours truly,

E. G. LOVE, *Librarian.*

It was ordered that the eighteen sets of the Journal now available be reserved to sell intact as sets.

The matter of the storage of the numbers of the Journal was referred to the committee authorized to make a new contract for printing the Journal.

The following motions with reference to the library were adopted :

*Resolved*, That a card catalogue of the library be prepared

under the direction of the librarian as soon as the work can be conveniently accomplished, and that the Directors be requested to appropriate for such purpose the sum of fifty dollars, or so much thereof as may be necessary, from funds of the Society not otherwise appropriated.

*Resolved*, That the Directors be requested to appropriate a sum not exceeding twenty-five dollars to furnish new shelving for the library.

*Resolved*, That a committee, consisting of the librarian and two other members of the Society, be appointed with power to eliminate useless matter from the library.

Upon motion of Dr. Hart, the Committee on Abstracts was discharged. The following resolution was then presented and adopted :

*Resolved*, That a committee of five be appointed by the chair to report at the annual meeting upon the advisability of preparing a title index of papers for the Journal.

The following motion was adopted :

*Moved*, That all nominees to membership up to the close of this meeting be considered as acted upon by the Council, and the secretary shall declare them elected whenever all the other requirements of the constitution in regard to them as nominees shall have been met.

A communication from Mr. Ewell, chairman of the Committee on Standards for Instruments of Measure, was presented, showing briefly what that committee has already accomplished.

Prof. John H. Long presented a communication from the Chicago Local Section inviting the Society to hold its winter meeting in Chicago. He most heartily urged the acceptance of the invitation which was renewed this year, and showed that while Chicago acquiesced last year in the decision that it was best for the Society to hold its winter meeting then in New Haven, yet this year he hoped that nothing would prevent the acceptance of the invitation, which was cordially renewed for the winter of 1900.

Upon motion, it was resolved that the cordial invitation extended by the Chicago Section to hold the next general meeting in the city of Chicago be and the same is hereby accepted with much pleasure. It was also resolved that the meeting be held

during the last week in December, and that the exact date for the meeting be fixed by the president and secretary.

After some discussion regarding qualifications for membership, it was voted that the Committee on Membership be requested to adopt a more liberal interpretation of that portion of the constitution which treats of this subject.

After some discussion of some other matters, upon which no action was taken, the Council adjourned.

ALBERT C. HALE, *Secretary*.

#### COMMITTEE ON TWENTY-FIFTH ANNIVERSARY.

Wm. McMurtrie, *Chairman*.

Albert C. Hale, *Secretary*.

H. C. Bolton,	A. A. Noyes,
C. L. Jackson,	C. E. Munroe.
J. H. Long,	C. F. Chandler,
Charles Baskerville,	S. W. Johnson,
W. L. Dudley,	A. B. Prescott,
H. H. Nicholson,	Ira Remsen,
W. B. Rising,	E. W. Morley,
W. P. Mason,	C. B. Dudley,
G. F. Barker,	C. A. Goessmann,
J. W. Mallet,	Henry Morton,
Jas. Lewis Howe,	C. A. Doremus,
J. H. Appleton.	

#### COMMITTEE TO ELIMINATE USELESS MATTER FROM LIBRARY.

E. G. Love,	E. E. Smith,
A. P. Hallock.	

#### COMMITTEE ON TITLE INDEX.

Wm. McMurtrie,	A. A. Noyes,
W. A. Noyes,	C. F. Mabery,
C. E. Munroe.	

#### NAMES PROPOSED FOR MEMBERSHIP.

Clark, Alfred N., Agricultural College, Mich.  
 Harrington, Charles, Harvard Med. School, Boston, Mass.  
 Harris, Isaac F., Chapel Hill, N. C.  
 Jürgensen, Dr. Rolof, care of Dr. Jürgensen and Bauschlicher.  
 Techn.-Bureau für die Chem.-Industrie, Prag-Zizkov, Austria.

Shepard, C. H., Pinole, Contra Costa Co., Cal.  
Smith, Lyman G., Roxbury High School, Warren St., Boston, Mass.  
Smith, Thorn, Isabella, Polk Co., Tenn.  
Wainwright, John W., 177 W. 83rd St., N. Y. City.  
Young, Clare C., 518 Alvarado, Los Angeles, Cal.

NAME PROPOSED FOR ASSOCIATE MEMBERSHIP.

Medcalf, George T., Box 280, Eureka, Humboldt Co., Cal.

NEW MEMBERS ELECTED JUNE 26, 1900.

Allen, Richard F., Hart Park, West New Brighton, S. I., N. Y.  
Hancock, Wm. J., Erasmus Hall High School, Brooklyn, N. Y.  
Logan, Lily, Howardsville, Va.  
Norton, (Mrs.) Alice P., 47 Hancock St., Auburndale, Mass.  
Richards, Alfred N., 437 W. 59th St., N. Y. City.  
Sundstrom, Carl, Solvay Process Co., Detroit, Mich.  
Sundstrom, Karl J., Trenton, Mich.  
Taylor, Thomas M., Oberlin, O.  
Torrey, Joseph, Jr., 8 Avon St., Cambridge, Mass.  
Waddell, John, School of Mining, Kingston, Ontario.

ASSOCIATES ELECTED JUNE 26, 1900.

Pretzfeld, Chas. J., 1211 Madison Ave., N. Y. City.

NEW MEMBERS ELECTED JULY 20.

Bolling, Randolph, V. I. C. & C. Co., Radford Blast Furnace, Radford, Va.  
Brown, Walter B., Nelson Morris & Co., U. S. Yards, Chicago, Ill.  
Diehl, Oscar C., Parke, Davis & Co., Detroit, Mich.  
Hall, Everett, J., Passaic, N. J.  
Hillyer, Homer W., Madison, Wis.  
Kniffen, Frederick, Indian Head, Ind.  
Lucas, Alfred, Survey Dept., Public Works Ministry, Cairo, Egypt.  
Lyons, Philip D., Md. Steel Co., Sparrows Point, Md.  
Nathan, Albert F., 603 Mumford Court, Kansas City, Mo.  
Reid, E. Emmet, College of Charleston, Charleston, S. C.  
Root, W. W., 186 Eugenie St., Chicago, Ill.  
Sears, Frederick S., St. Paul's School, Concord, N. H.  
Seward, George O., Holcomb Rock, Va.

Walker, Claude F., Calumet, Mich.  
Wiley, Walter B., Bramwell, W. Va.  
Willcox, Frank A., Oakland, Bergen Co., N. J.

ASSOCIATES ELECTED JULY 20, 1900.

Calvert, Joseph E., Etna, Allegheny Co., Pa.  
Condit, Louis C., 139 Lafayette Ave., Brooklyn, N. Y.  
Kohnstamm, Lothair S., 133 E. 71st St., N. Y. City.  
Thomas, T. Lewis, 71 Broadway, N. Y. City.  
Warren, Robert, S. 6th St., Terre Haute, Ind.

CHANGES OF ADDRESS.

Archibald, E. H., Harmony, Colchester Co., Nova Scotia.  
Enright, Bernard, 330 E. 4th St., So. Bethlehem, Pa.  
Johnson, Treat B., Westville, Conn.  
Langmuir, A. C., care of Mark & Rawolle, 9 Van Brunt St.,  
Brooklyn, N. Y.  
Lipman, J. G., Woodbine, N. J.  
Quinan, W. R., Guardian Bldg, Cape Town, So. Africa.  
Rising, H. R., 39 S. 10th St., Newark, N. J.  
Rolfe, Geo. W., 1 Cleveland St., Cambridge, Mass.  
Scherr, E. W., 230 W. 113th St., New York City.  
Shorey, Edmund C., Box 360, Honolulu, H. I.  
Walker, Percy H., 416 McClury St., Huntsville, Ala.

Issued with September Number, 1900.

## Proceedings.

### COUNCIL.

#### NAMES PROPOSED FOR MEMBERSHIP.

Hegeman, John W., 102 Barbey St., Brooklyn, N. Y.  
Hooper, Everett D., 10 Studio Building, Boston, Mass.  
Porter, Horace C., 902 Locust St., Kansas City, Mo.

#### CHANGES OF ADDRESS.

Enright, Bernard, 330 E. 4th St., South Bethlehem, Pa.  
Goldstein, Harris, care J. W. Preston, Tyler St., Depew, N. Y.  
Hibbard, P. L., 525 Clayton St., Waukegan, Ill.  
Kendall, E. Dwight, 1109 Park Pl., Brooklyn, N. Y.  
Leach, Miss Mary F., 74 Pitcher St., Detroit, Mich.  
Lenher, Victor, Univ. of Wisconsin, Madison, Wis.  
Stursberg, J. A., care W. Stursberg, Schell & Co., 79-81  
Leonard St., N. Y. City.  
Thompson, Firman, New Carlisle, O.  
J. V., Pekin, Ill.

#### ADDRESS WANTED.

Welt, Miss Ida, formerly of 814 Lexington Ave., N. Y. City.

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### MEETINGS OF THE SECTIONS.

#### RHODE ISLAND SECTION.

The annual meeting of the Rhode Island Section of the American Chemical Society was held June 13, 1900, at Kingston, R. I.

The Section was entertained by Dr. J. H. Washburn, president of the Rhode Island College of Agricultural and Mechanical Arts.

The following officers of the Section were elected for the year 1900-1901 :

Presiding Officer, Walter M. Saunders ; Secretary and Treasurer, Walter E. Smith ; Member of the Executive Committee, Charles M. Perry.

WALTER E. SMITH, Secretary



Issued with October Number, 1900.

## Proceedings.

### COUNCIL.

#### NAMES PROPOSED FOR MEMBERSHIP.

Hicks, Walter T., 300 S. Broadway, Los Angeles, Cal.  
Johnson, Charles M., 701 Orchard St., Avalon, Pa.  
Rademacher, Hermann A., Box 243, Lawrence, Mass.  
Rogers, Herbert F., Provident Chem. Wks., St. Louis, Mo.  
Vosburgh, C. H., High School, Jamaica.

#### NEW MEMBERS ELECTED AUGUST 24, 1900.

Harrington, Charles, Harvard Med. School, Boston, Mass.  
Harris, Isaac F., Chapel Hill, N. C.  
Jürgensen, Dr. Rolof, care Dr. Jürgensen and Bauschlicher,  
Tech.-Bureau für die Chem.-Industrie, Prag-Zizkov, Austria.  
Shepard, C. H., Pinole, Contra Costa Co., Cal.  
Smith, Lyman, G., Roxbury High School, Warren St., Boston, Mass.  
Smith, Thorn, Isabella, Polk Co., Tenn.  
Wainwright, John W., M.D., 177 W. 83rd St., N. Y. City.  
Young, Clare C., 518 Alvarado, Los Angeles, Cal.

#### ASSOCIATE ELECTED AUGUST 24, 1900.

Medcalf, Geo. T., Box 280, Eureka, Humboldt Co., Cal.

#### CHANGES OF ADDRESS.

Adams, Maxwell, 5815 Drexel Ave., Chicago, Ill.  
Best, Otto, Bay & Dupont Sts, San Francisco, Cal.  
Brown, H. F., Int. Sm. Powder & Dynamite Co., South Amboy, N. J.  
Culmann, Julius, 400 W. 153rd St., N. Y. City.  
Dailey, J. Glanding, care Ledoux & Co., 99 John St., N. Y. City.  
Goldstein, Harris, 228 Henry St., N. Y. City.  
Grabfield, Jos. P., Medinah Temple, cor. Jackson and 5th Ave., Chicago, Ill.  
Hummel, John A., Agr. Expt. Sta., St. Anthony Park, Minn.

Kendall, Robert E., 46 Maple St., Glens Falls, N. Y.  
Loeser, R. M., Palo Alto, Cal.  
Mabery, C. F., 57 Adelbert St., Cleveland, O.  
Moyer, J. Bird, 5116 Arch St., Philadelphia, Pa.  
McKenzie, R. Monroe, Rahway, N. J.  
Peppel, S. V., 169 King Ave., Columbus, Ohio.  
Phalen, W. C., Socorro, N. M.  
Sovereign, C. L., Glucose Sugar Ref. Co., Davenport, Iowa.  
Tucker, Chas. W., Grant & Farragut Roads, Swampscott,  
Mass.  
Tufts, J. L., Gen. Chem. Co., Laurel Hill Works, Laurel  
Hill, N. Y.  
Walker, Percy H., Fayetteville, Ark.

ADDRESS WANTED.

Goodell, George A., formerly of 284 St. Nicholas Ave., N. Y.  
City.

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ERRATUM.

By an oversight the name of Dr. Talbot did not appear in the list of councilors present at the meeting of the council in New York last June. He was present, and his name should be added to the list of those councilors who attended the meeting.

## Proceedings.

### COUNCIL.

The motion printed on page 74 of the Proceedings has been amended so as to read as follows :

*Resolved*, That the president of the Society appoint a committee of five, of which he himself shall be one, to report to the Council upon a new contract for the printing of the Journal of the Society.

It has also been voted that the present contract for printing the Journal be continued till such time as a new contract can be presented and approved.

### NAMES PROPOSED FOR MEMBERSHIP.

Balcom, Reuben W., Mass. Inst. Tech., Boston, Mass.  
Baltzly, Edwin B., Perth Amboy, N. J.  
Benedict, Francis G., Middletown, Conn.  
Braman, Winfred W., Durham, N. H.  
Breves, Rudolph, Rahway, N. J.  
Brown, John W., 126 Massachusetts Ave., Boston, Mass.  
Champion, E. C., Iola Portland Cement Co., Iola, Kans.  
Gordon, A. S., Oliver Iron Mining Co., Mountain Iron, St. Louis Co., Minn.  
Grainger, Wm. E., Cranberry, Mitchell Co., N. C.  
Hemmings, Frederick J., 12 Pearl St., Boston, Mass.  
Heckeroth, Wm. C., 3443 N. 18th St., Philadelphia, Pa.  
Heckman, J. Conrad, Larkin Soap Co., Buffalo, N. Y.  
Melcher, Arthur C., 58 Bowen St., Newton Centre, Mass.  
Morgan, W. C., Washburn College, Topeka, Kans.  
Osgyani, Arpad, 64 Orchard St., Astoria, L. I., N. Y.  
Pough, Francis H., 146 Hicks St., Brooklyn, N. Y.  
Walton, James H., Jr., Room 317, 126 Massachusetts Ave., Boston, Mass.  
Wheeler, Alwyn S., Chapel Hill, N. C.  
Woods, Chas. D., Orono, Me.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Cary, Edward A., Lafayette College, Easton, Pa.  
Felt, W. W., 9431 Normal Ave., Chicago, Ill.  
Haskell, Albert A., Essex, Mass.  
Howard, John J., 118 McKeen Hall, Easton, Pa.

NEW MEMBERS ELECTED SEPTEMBER 17, 1900.

Hegeman, John W., 102 Barbey St., Brooklyn, N. Y.  
Hooper, Everett D., 10 Studio Bldg., Boston, Mass.  
Porter, Horace C., 902 Locust St., Kansas City, Mo.

CHANGES OF ADDRESS.

Affelder, Oscar I., 1230 Sheffield St., Allegheny, Pa.  
Archibald, Eben H., 1691 Cambridge St., Cambridge, Mass.  
Ashley, Harrison E.; care Tremont Nail Co., West Wareham, Mass.  
Barrows, W. A., Jr., Everett, Bedford Co., Pa.  
Baxter, Gregory P., Swarthmore College, Swarthmore, Pa.  
Beans, H. T., Univ. of Idaho, Moscow, Idaho.  
Bonnet, Frederic, 9 Wadsworth House, Cambridge, Mass.  
Bowman, Walker, 538 W. 14th St., New York City.  
Cayvan, L. L., 294 W. Monroe St., Chicago, Ill.  
Chesnut, Victor K., U. S. Dept. of Agr., Washington, D. C.  
Condit, Louis C., 85 Newkirk Hall, Lafayette College, Easton, Pa.  
Cook, A. D., 519 E. State St., Ithaca, N. Y.  
; Craig, A. G., 5803 Parker St., Pittsburg, Pa.  
Cuadrado, Gaston A., Dept. de Anal. Quimico, Monte 44, Habana, Cuba.  
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ROBERT WILHELM BUNSEN.



## PROFESSOR R. W. BUNSEN.

The committee<sup>1</sup> appointed at the Columbus Meeting of the American Chemical Society to draw up a memorial upon the late Professor R. W. Bunsen, an honorary member of the Society during nearly the whole period of its existence, presents the following as a tribute of the Society and of American chemists generally to the life, character, and works of that great man and eminent chemist.

Robert Wilhelm Eberhard Bunsen was born in Göttingen on March 31, 1811. Among his ancestors one of the most prominent was Jeremiah Bunsen, who lived in Arlosen, 1688-1752, and was Hofmaler, Münzmeister, and Bürgermeister there. He was a great admirer of natural science, and himself published certain writings on electricity, magnetism, the Northern Lights, etc.

Little is known of Robert Bunsen's childhood and youth. He was the youngest of four sons of Christian Bunsen, librarian and professor of philology in the University of Göttingen. The father was a man of cheerful disposition and a ready sense of humor. His mother was the daughter of a British officer of Hanover,—Quensel,—a woman possessed of depth of mind and heart. It is not difficult to see that some of the characteristics of both parents were freely transmitted to the son. As a boy, Bunsen is said to have been of a quick and violent temper, which his mother only knew how to control, but those who knew the man could scarcely be brought to give credence to such rumor. If true, however, how great must have been the self-mastery that changed him into the serene and quiet man of his mature years! At home Bunsen had excellent opportunities to learn languages other than his native tongue, from the number of foreign youths, especially French, who frequently visited his parents and sometimes lived in the family. This was a very fortunate circumstance and early became of great practical utility to him. At the age of seventeen he passed his matriculation examination for the University, and when nineteen took the degree Doctor of Philosophy. He had a good classical education and even to his old age was fond of reading Cicero and other Latin authors in the original. In 1830 he won an academic prize for an exhaustive enumeration and description of hygrometers, written in elegant Latin. This paper seems also to have served as his inaugural dissertation upon the attainment of his doctor's degree.

At the University he was quiet and retiring and took but little

<sup>1</sup> The committee has made free use of every available source of information regarding Professor Bunsen, and has endeavored to give credit for all important quotations, although it has not seemed necessary to indicate with quotation marks simple data of statistics and facts.

part in what is generally understood as student life. He was full of good humor, however, and a diligent and enthusiastic student. His special subjects of study were physics, chemistry under Stromeyer, mineralogy and geology under Hausmann, and mathematics under Gauss. He was especially fond of geognostic studies and made frequent excursions in the vicinity of Göttingen and in the Harz. These excursions for practical study and observation he began even before he entered the University.

In May, 1832, Bunsen undertook an extended tour for the sake of broadening his scientific information and culture. He went to Berlin, Paris, and Vienna, making a large portion of the journey afoot, visiting chemical manufactories and other works at various points en route, and taking many opportunities to extend his geognostic observations. During this tour he formed the acquaintance of many of the leading scientists of his day, and enjoyed more or less intimate association with a number of them. He met Runge, Gustav and Heinrich Rose, and Mitscherlich, and was with the latter for three weeks pursuing geognostic studies in the Eifel. In Giessen he met Liebig and Wöhler, and in Paris Pelouze, Regnault, Brogniard, and others. He studied the mineral and geological collections of Weiss and for a time worked in the laboratory of Heinrich Rose. It was under the advice of Rose that he went to Paris. While in Paris he attended a session of the Academy at which Chevreul, then at the summit of his fame, presented a paper upon cholera and its treatment. At this session also it was announced that Ampère had found in hydrofluoric acid a specific for combatting the disease. Bunsen, through the recommendation of prominent scientists, gained admission to the Polytechnic School, where he attended a course of lectures during the winter semester, 1832-1833. He made no attempt to attend lectures in Berlin and Vienna, but preferred to extend his scientific knowledge and opportunities by acquaintance and association with the learned men whom he met. In this he succeeded to a remarkable degree, and he dated a life-long acquaintance and deep friendship with Heinrich Rose, Mitscherlich, and others from this tour. He remained in Paris from the last of September till the middle of May and then went to Vienna *via* Innsbruck and Salzburg. His stay in Vienna lasted about six weeks, after which he returned to Göttingen, stopping on his way at Prague, Freiberg, and Leipsic.

The object of Bunsen's tour had been most successfully attained. He had come into personal acquaintance with great scientists of Europe, and by their aid and friendship had had opportunities for the study of theoretical and applied science, which helped to lay broad, deep, and solid the foundation upon which his success and fame were to be built. Already he was a

marked man and many eyes were looking toward his future. Returning to Göttingen, he became privatdocent in 1833, and after three semesters, upon the death of Stromeyer, he conducted the lectures at the University upon theoretical and practical chemistry. His popularity was great, as was shown by the number of students in attendance. In January, 1836, Wöhler was called to become the successor of Stromeyer, at Göttingen, and Bunsen was appointed Wöhler's successor as professor of chemistry in the Polytechnic School at Kassel. This institution had long been known for the character and standing of its professors, and Bunsen did his part in sustaining its reputation. He entered upon his work at Kassel with great vigor and made an enviable record during the short period of his stay there.

In 1838, Bunsen accepted a call to the University of Marburg, where he remained thirteen years as professor and director of the chemical laboratory. In 1851, he went to the University of Breslau, where he planned a famous working laboratory, and the next year he accepted a call from Heidelberg, at that time the goal of every German professor's ambition, and "the *ne plus ultra* of his promotion." Here he planned a new laboratory which, when completed in 1855, was the largest in all Germany, furnishing working places for fifty students. Here it was that students from all quarters of the world thronged and crowded upon one another to secure the opportunity of attending the lectures and obtaining personal instruction in laboratory practice and research from the now renowned professor. Bunsen remained at Heidelberg until the day of his death, repelling all overtures from Berlin when the German government was putting forth its most strenuous efforts to make the university of that city the greatest seat of learning in all Europe. He retired from active work in 1889, having filled the position of teacher for more than fifty years, during which period all his important work as a scientist was also accomplished. His death occurred August 16, 1899.

In 1834, Bunsen, in conjunction with his colleague Berthold, published the results of his first scientific investigation, and by that means conferred a lasting boon upon humanity. He announced that moist, freshly precipitated ferric hydroxide is a sure antidote in cases of arsenical poisoning, providing it is given early enough and in sufficient quantity. This paper at once attracted wide attention on account of the great and permanent importance of the remedy which is to-day almost universally known and accessible.

In 1835, Bunsen investigated some of the compounds which the double cyanides form with ammonia. He measured the angles of the crystals which many of the cyanides form and estab-

lished certain facts contrary to the general belief regarding these compounds. He showed, *e. g.*, that ammonium ferrocyanide is not produced by boiling Prussian blue with ammonia, but by digesting ammonium carbonate with lead ferrocyanide.

Closely following these early investigations came Bunsen's important researches upon the cacodyl series of organic compounds, which contributed largely to the establishment of the theory of compound radicals and gave to the world the first example of an organo-metallic body, or, as Bunsen called it, "a true organic metal." These researches covered a period of five years, from 1837 to 1842, and constituted his only great and important excursion into the field of organic chemistry. The preparation and study of the properties of cacodyl were attended with the greatest risks; the safety and even the life of the investigator were in almost constant jeopardy. "One cannot read the memoirs describing the preparation of this compound without being impressed with the difficulty of the task, the attendant danger, and the ingenuity displayed in conducting the investigations." "A highly poisonous liquid, very volatile, dangerously explosive, spontaneously inflammable in the air," and insupportably offensive to the smell, this fearful compound taxed all the resources of the investigator and proved to the world the stuff he was made of. But even Bunsen, "with his scientific acumen and unflinching determination, did not escape scot-free from such a labor, for in analyzing the cyanide of cacodyl the combustion-tube exploded and he lost the sight of an eye and for weeks lay between life and death, owing to the combined effect of the explosion and the poisonous nature of the vapor." Upon regaining his strength, however, he continued his investigations with unremitting vigor. His patient persistence and courage were sublime, and his superiority to conditions and emergencies and the final results of these labors convinced the world that a master hand and brain had been engaged in wresting from nature some of her subtlest secrets.

At Marburg, Bunsen made a study of the chemical changes which occur in the blast-furnace. In 1838, he proved, by accurate analyses of the gas escaping from the furnace used in connection with the hematite iron mines there, that at least 42 per cent. of the heat from the fuel was lost in the escaping gases. He showed how these gases could be collected and utilized as fuel and thus far greater economy and efficiency obtained in working the furnace. Besides "pointing the way to a method of economical working without which probably but few ironmasters of the present day could exist," he devised methods of gas analysis which were far in advance of those of Priestley, Cavendish, Gay-Lussac and others and which form

the basis of the exact gas analysis of to-day. Roscoe, in 1881, said of this work: "This important branch of analytical chemistry has been created and brought to its present wonderful degree of precision solely by the head and hands of the Heidelberg experimental philosopher." His investigations of gases were not confined, however, to analytical methods and technical applications. He did pioneer work also in the study of the constants of gases. His researches on the laws of gaseous diffusion and their application in gas analysis, on the phenomena of the combustion of gases, the temperature of ignition, measurements of specific gravity, coefficients of absorption, etc., were conducted with characteristic zeal and devotion. Not content with the range of his investigations, he visited Vesuvius in Italy and the volcanic region of Iceland, and collected the gases issuing forth from hot springs. With the data he had obtained, he formed his theory of the inner construction of the earth, volcanic eruptions, and the action of geysers.

Besides his investigations of the gases and the phenomena of volcanic and geyser action, Bunsen collected samples of volcanic rocks during his trip to Iceland, and later, in 1853, made careful analysis of these, deducing from his results conclusions upon which he based his theory of the composition of volcanic rocks.

In 1841, Bunsen invented the well-known voltaic cell in which carbon was substituted for the expensive platinum as the negative electrode. This at once took rank as the most economical and efficient means for obtaining a powerful electric current, and remained such till the invention and perfection of the dynamo.

With the aid of his voltaic cell, Bunsen began investigations on the electrolytic reduction of magnesium from its chloride. By this means he was able to produce that metal on a scale never before known, and by pressing it into wire used it later in his investigations on the chemical activity of light. The prominence thus given to this metal led to its commercial production soon afterwards. A detailed account of Bunsen's important electrolytic work would be very voluminous. Chromium, aluminum, manganese, alkalies and alkaline earths were reduced, and many of the rare metals were isolated and their atomic weights and other constants so accurately established that many of these determinations are still regarded as authoritative. The reduction of the alkaline earths was made in conjunction with Dr. Matthiessen, and the metals of the cerium group were investigated with Norton and Hillebrand.

Bunsen used his voltaic battery in an entirely different way also in studying the properties of metals. He made an arc-light,

with the different metals as electrodes, and analyzed the light with a prism. In that way, in 1844, some years before the invention of the spectroscope, he obtained and described the true line spectra of various elements. For many years after this, Bunsen's investigations in spectrum analysis were interrupted by other matters, and when he renewed his researches in this direction, it was with the aid of the gas-burner which he had meanwhile devised, and later with the additional aid of the spectroscope, the joint production of the inventive genius of himself and his colaborer, Kirchhoff.

In 1857, Bunsen and Roscoe first described the Bunsen burner. This invention furnished a non-luminous gas flame, of relatively high temperature, in which chemical substances could be vaporized and a spectrum obtained due to the luminous vapor. This burner is now used as a source of heat in various manufacturing processes, and in many households, and is practically indispensable in all chemical laboratories. With the invention and use of this burner, a new impulse was given to the investigation of the spectra of the metals, and Bunsen now studied them from their chlorides, as these were volatilized in the colorless flame of the burner. Kirchhoff, professor of physics at Heidelberg, became associated with him in these researches, and dealt more especially with the physical problems involved, while Bunsen approached the subject from the standpoint of a chemist who was also an expert in various phases of physical research.

In 1859, Bunsen and Kirchhoff perfected the spectroscope and continued their classical researches in spectrum analysis, among other results discovering the metals caesium and rubidium, the salts of which were obtained in small quantity, but in the hands of Bunsen in sufficient amount to enable him to determine many of the properties and constants of these rare metals. By evaporating 44,000 kilos of the Dürkheim mineral water in which traces of these two metals had been found, he obtained 16.5 grams of the mixed chlorides of the two new metals, and with this he succeeded in separating them and in establishing their relationship so well that his results still stand as practically correct and complete.

The invention of the spectroscope, the founding of the science of spectrum analysis, and the important researches in that science which were conducted by Bunsen and Kirchhoff, led to far-reaching results and were alone sufficient to place the name of each of these investigators upon the pinnacle of enduring fame. From the record that has already been made by this new method of research, we are warranted in saying that it would require the boldest flights of scientific imagination



to encompass the variety and extent of the uses to which the spectroscope may be applied and of the revelations which may be expected from spectrum analysis. In fact it has already thrown floods of light upon nearly every department of theoretical science and has furnished one of the keenest and most penetrating of instruments which man can use in the application of science to practical affairs, and to the investigation of unexplored fields of scientific research. A catalogue of its revelations in optics, astronomy, and chemistry and of its application in medical and medico-legal practice and in the arts and manufactures, would be wearisome from the mass of important details it would present, and we can best leave this topic by assuming that its principal facts and outlines are to-day familiar to every well-informed person.

Bunsen's work in connection with the spectroscope and spectrum analysis constituted only a portion of his researches upon light. Just as the investigations of the line, absorption and spark phenomena were of far-reaching scientific importance and have been turned to practical account in a great variety of directions, so his researches upon the chemical action of light have been regarded as "the classical model for all later investigations in the realm of physical chemistry" and have been of great practical value in considerations affecting photography, agriculture, and various other arts and industries, while his method of measuring the intensity of light from any given source, is of great importance from a scientific standpoint and has its valuable application in the Bunsen photometer as used to-day in determining the candle-power of illuminating gas and the electric light.

The variety and accuracy of Bunsen's analytical methods are marvelous. It has been said that "next to Heinrich Rose he was the greatest and especially the most original analyst of his time." There are those, however, who would not make even this exception in favor of Rose, especially when Bunsen's manipulative skill, the certainty and accuracy of his results, his many ingenious devices, and the simplicity of the apparatus he designed for doing his work are taken into consideration. We have only to mention his gasometric and volumetric methods, his flame reactions, distinct from the spectrum analysis, his analyses of silicates and mineral waters, separation of arsenic and antimony, separation of the rare earths and the metals of the platinum group, to recall these and scores of other processes with which every chemist is to-day familiar, which he employs in his own work whenever occasion may arise and for many of which no adequate substitute is yet known.

No important branch of chemistry remained unexplored by

Bunsen, and his accomplishments in any one of them alone would have secured for him abiding fame. Organic, inorganic, physical, analytical, theoretical, and technical chemistry were alike enriched by his researches and his name is connected in some way with our knowledge of almost every element known in his day. Chemical and other scientific laboratories to-day are full of apparatus and contrivances invented by Bunsen, and they have become practically indispensable in many lines of modern scientific research. No chemist or physicist now would think of carrying on his investigations without them. But the realms of chemistry and physics were not broad enough to circumscribe the genius and labors of Bunsen. He enriched every field which he entered as a scientific investigator and he entered fields of investigation in nearly every science. Chemistry, physics, and mineralogy, it is true, absorbed the greater portion of his time, thought, and energy, but the results he achieved in these were so fundamental and far-reaching that astronomy and various other branches of pure and applied science reaped a full and rich harvest as the ripened fruit of his labors.

It has been said that "it never once happened to Bunsen to take up any considerable research without producing a discovery decidedly brilliant; and he almost always flung in something useful to boot." This was eminently illustrated by his researches on cacodyl and the discovery of ferric hydroxide as a remedy for arsenical poisoning; by his analysis of blast-furnace gases, revealing the waste of gaseous fuel and pointing the way to more economical working through the use of the hot blast and the development and use of producer gas; and by his investigations in the realm of optics, leading to the invention of the spectroscope and the valuable results which have flowed from spectrum analysis.

Bunsen was a scientific genius of the highest order, whether we define the term genius as the capacity for work, or as the ability to perceive and recognize truth and bring to light fundamental facts and laws when buried beneath the rubbish of false theory and tradition or concealed by a mass of details which permit none but the most penetrating intellect to discover them and to bring them to the comprehension of ordinary minds and within the range of ordinary human experience. He was not himself very tolerant of theories. He said, in 1871, to one of his pupils, that he had already lived through three or four sets of theories and he expected to see many more before he died.

Bunsen used almost every discovery and investigation he made as a basis for further work, and it seemed as though every advance opened to him vistas ever more and more alluring. The good uses to which he put his battery and burner, the employment



of magnesium in his investigations on light and the thoroughness with which he worked out the properties of the metals he reduced, and various data regarding them, all testify to the completeness and comprehensiveness of his work. He never left much for others to do in the fields in which he labored. "He left the theme he chose completed." While following up a single line of investigation, he would often stray into by-paths in which he would pluck the ripened fruit with which nature tempted him, and strengthened and inspired by that he would return with broader data and fuller insight into the main line of his investigations as a reward for his little side trip. Many a person would have been distracted by the varied secrets which nature yielded to him at such times and might have been turned from the main subject of their inquiry by inviting side issues; but while Bunsen gave much attention to these, they always strengthened him in his main work while, at the same time, yielding abundant harvests and furnishing both the incentive and the foundation for subsequent investigations in kindred lines.

Bunsen's methods were precise, accurate, and thorough. His fondness for mathematics and his early education under Gauss in that direction, gave a decidedly mathematical turn to all his researches, and even the simpler reactions of the chemical laboratory were regarded by him from a mathematical point of view. This method of looking upon his work did not invest the subjects with greater obscurity, but just the reverse. The harmonious and fundamental relations of mathematics illumined the whole subject he was investigating, and so clarified the atmosphere as to render his methods charmingly simple and accurate. One can hardly say whether his mind was more successfully inductive or deductive in its processes. There was in its working a rare and happy facility in the use of both, and such a combination of them as rendered his investigations intuitively clear and direct, yet fundamental and comprehensive, and such as would satisfy the demands of formal deductive reasoning. His manipulations, methods of analysis, and construction of apparatus were but the outward and natural expression of the operations of his comprehensive and penetrating intellect.

Bunsen's greatness as a man and as a personal companion and friend is in no danger of being eclipsed by his world-wide renown as a scientific investigator, so long as the testimony of those who knew him can be called in evidence. Physically he was over six feet in height, of massive proportions and swarthy complexion. His personal address was so cordial and unaffected and the charming smile which illumined his features so capti-

vating that all whom he met were irresistibly drawn to him and loved to linger in the atmosphere of his presence. His pupils almost worshiped him for his genius and achievements, loved him for his fatherly ways and his interest in them and their work, and were frequently drawn into the closer relation of personal friendship by his generous nature and the childlike simplicity of his manner. In some instances these relations were lifelong and intimate, but whether circumstances rendered this possible or not, the kindest feelings of affection for Bunsen as a man, and a high estimate of his genius as a scientist and a teacher, were the permanent possession of those who worked with him in the laboratory and attended his lectures. "In that epoch-making book in literature and science entitled 'Heat as a Mode of Motion,' one of his former pupils has recorded his appreciation of Bunsen in the following language: 'To his friend and teacher, Robert Bunsen, this book is dedicated by John Tyndall.' " Roscoe, who, while a pupil, was very intimately associated with Bunsen in his investigations on light, says: "It is only those who have had the benefit of working under and with him who can fully understand the feeling of affection and respect with which his pupils regard his memory."

From some of his American pupils we quote the following expressions of appreciation, reminiscences, and estimates of Bunsen and his work :

"His name is dear and sacred to us all."

"I shall never forget his kindly patience and helpfulness. That sweet smile of his is ever present with me."

"I shall always remember with pleasure his fatherly ways and great interest in his pupils."

"I have many of the pleasantest recollections of the dear old gentleman who was most kind and gracious to me both in and out of the laboratory."

"To those whose good fortune it was to become an intimate, his nature unfolded, and close and devoted friendships were formed."

"His unaffected simplicity, genial nature, and most lovable disposition were marked characteristics which no one who came in contact with him as a pupil could fail to note. His interest in the work of his pupils was intense and sometimes manifested itself in unexpected ways. He was at all times an honest, faithful, and earnest searcher after truth, and never seemed conscious of any feeling of superiority over his humblest pupil. To know him was to love him. It would, indeed, be difficult to tell which feeling would be uppermost in one's memory of this truly great yet distinctly childlike man—admiration for his achievements or veneration for his character."

“ Nothing could win a student's heart more quickly than the gracious way in which he would initiate the beginner into flame reactions, except it might be the delight it gave him to conduct an advanced student through the mazes of a mineral water or platinum ore analysis, or the charm he would throw about his methods of exact measurement, as in the graduation of a eudiometer, the making of an elaborate gas analysis, the determination of the specific heat of a solid, liquid, or gas, or the mapping of spectra.”

“ I could write of the enthusiastic reception of Professor Bunsen by his students as he appeared at the door of his lecture room, the inspiration his presence made as he gave suggestions at the laboratory tables, his marvelous skill in chemical manipulations, his simple, patient way of illuminating for a student what had been an obscure subject, the crisp words of commendation for a bit of good work done, the feeling near to worship that came to his pupils; but these facts are, I suppose, the common knowledge of all his students.”

“ As a student I felt I was alongside of a kind-hearted big boy who knew immensely more than I did, and was only too anxious to help me in need. We felt he was interested in our work and was not only capable of assisting us but was ready at a moment's call to help and to advise. I felt that I was getting from him far more personal attention than I deserved. He was one of us in our working hours and was anxious to bring each labor to a successful result. He lost nothing in professional dignity thereby. We never presumed at familiarity. To us he was ever Robert Bunsen, Geheimrath, and we kept our places 'with our hands on our mouths and our mouths in the dust.' ”

“ As to the inspiration I derived from two semesters of close contact with him, it was worth all my years elsewhere.”

“ He was a prince among teachers, simple, plain, and clear, and admirable in his experimenting. The only notes he used were mathematical data written upon a small blackboard at his left hand. In the working laboratory he was always patient and gave us personally a great deal of attention, more than we got anywhere else.”

“ I first met Bunsen in the retired valley of Engelberg, Switzerland, in 1863. Learning by accident that he was at an adjoining Gasthaus, I called on him and told him of my plans to continue my studies in Heidelberg. He received me graciously and immediately won my heart by his affability, by the charming smile that lit up his large features, and by his unselfish interest in my personal affairs.”

“ I first met Professor Bunsen, November 6, 1855. I had gone to Germany to study chemistry under him and Liebig, and the

day of my arrival at Heidelberg I called on him at his rooms in the new laboratory building. This was then considered the largest and best arranged in the world. I found him smoking his after-dinner cigar and I immediately took a liking to him. He was then in the prime of life, forty-four years old, and his genial but earnest face impressed me. He seemed younger than I had expected. He had many questions to ask about chemical instruction in America, for students from this country were then flocking to the German University. There were then between fifty and sixty students in his laboratory, scarcely more than half of them German. It seemed to me that half of the nations of the world were represented. Bunsen was genial with his students, visiting everyone's table in his daily circuit of the working rooms, having something to say to each one about his work, even if but a word, but would generally linger if properly tempted. He gave his lecture on general chemistry at nine o'clock in the morning. His method was clear, logical, and concise. He would begin his lecture from the standpoint of our present knowledge of the subject he was discussing, commencing with the element and following by logical succession the chemistry of its compounds."

"Just after the Christmas recess he invited his students to a dinner at the Badischer Hof. It was a happy occasion. There were a few short speeches and he seemed doubly genial. In those days a good cork was a prize for laboratory use, and when on that occasion he caught me slipping a champagne cork into my pocket, with a twinkling eye he remarked that I had the true laboratory instinct. As the dinner broke up he carefully gathered up and carried the other champagne corks away in his pockets, remarking to a student that champagne corks should never be wasted."

"At the opening of my third term, I was elected 'Polizei.' One of the events of my official life was regarded as an exhibition of unparalleled audacity of which only an American was capable. I fined Hofrath Bunsen, who, after lighting his cigar at the flame of a Bunsen burner, had left the gas burning and gone out of the room. According to custom and much to the consternation of the students, I chalked on the desk that Bunsen had used, the words 'six kreutzers' over my initials—a notice that could not be erased until the fine was paid. The next day when Bunsen approached the desk, he glanced at the inscription, smiled broadly, and to the amusement of the crowd of students that had gathered to see the result of my daring, opened his purse and handed me six kreutzers, with a pleasant commendation of the fidelity of the 'Polizei.'"

"After every lecture Bunsen rarely missed spending several

hours in the laboratory, going from student to student with inquiries, suggestions, and useful hints. Desirous of securing my share of this personal contact, I soon found the best way of inducing the Hofrath to linger was to have a supply of clean test-tubes and beakers on an orderly desk, with a query or two requiring experimental answers."

"While Bunsen rarely met his students outside the laboratory, he captivated each by the deep personal interest he took in their individual work. Indeed, so intense was his devotion often to their themes that it was not uncommon for a pupil to find on coming in the morning an analysis or process several stages more advanced than when it was left the night before. Bunsen was an early riser as well as a late worker, and between the two found ample time to have a 'finger in the pie.'"

"Bunsen's practical side is best known to the average man. He was a craftsman beyond compare in the details of what was needed in laboratory utensils and manipulative skill, as was evinced by simplicity of construction, neatness of procedure, and accurateness of result."

"As to his contributions to chemistry, they were enormous, and you must bear in mind that he was born in 1811 and that many of the devices of the laboratory, and most of the principles of the science of chemistry which we are teaching now as a sort of matter of course, 'things that go without saying,' were utterly unknown when he was graduated in Göttingen in 1830."

"In everything Bunsen attempted he was never satisfied until he had finished his work and put it upon an exact scientific basis. I have good cause to think him the best teacher I have ever had and the best chemist of his generation."

"Bunsen became an integral part of Heidelberg and the prestige of this university was to a considerable extent dependent upon his individuality. It was at this seat of learning that he made his most important discoveries and drew men from all parts of the world to his laboratory. Admirable as his previous work had been, it was amidst the charming natural surroundings there and in daily contact with such minds as Helmholtz, or his devoted coworker Kirchhoff, or in the genial companionship of Kopp and Hesse that his genius expanded. It was quite in keeping with his nature that others should partake of the infinite pleasure he had experienced, and he gladly initiated them into the skilful methods his resourceful mind had developed."

"Nothing so much marks Bunsen as a chemist of a past generation as the fact that one cannot speak of him as especially distinguished in any particular branch of the subject. If we go over the men of our science who are well known to-day we find that nearly every one is very closely identified with organic,

analytic, physical, or some other department of chemistry, and has done very little of note outside of his particular field. Bunsen did so much valuable work in every branch of chemistry that he was distinguished in all."

LIST OF AMERICANS WHO HAVE STUDIED UNDER PROFESSOR R.  
W. BUNSEN.

The following list is, beyond doubt, incomplete, especially as to those who simply attended Bunsen's lectures without working in his laboratory, as was a common custom with medical students in particular. An attempt has been made to communicate with each living person whose name appears in the list. In a number of cases the letters of inquiry have elicited no response, and the information, obtained at second-hand and often meager, has thus been impossible of verification or extension. It is believed, however, that so far as concerns those who at one time or another worked in Bunsen's laboratory, the list is nearly complete.

Of the 101 persons enumerated at least 62 have either taken the doctor's degree under Bunsen or have at one time or another filled professional chairs at one or more institutions of learning, or both. Of the above 62, there are known to have taken the degree 33, and to have become professors 46. A number of the latter took their doctor's degree elsewhere. Death has claimed at least 20.

Andrus, Geo. Lawrence. (Brooklyn, N. Y.) 1873-74. Present address unknown. Did not pursue chemistry as a profession.

Austin, W. Lawrence. 1871-74. Ph.D., 1876. Metallurgical engineer, Denver, Colo. (Box 941).

Bache, Chas. L. 1869-71. Formerly with Philadelphia mint; now assayer and metallurgist, Redding, Cal.

\*Bayne, H. A. 1875. At one time professor of chemistry, Royal Military College, Kingston, Ontario, Canada.

Becker, Geo. F. (New York.) 1868-69. Ph.D., 1869. Graduate Royal School of Mines, Berlin, 1871. Instructor University of California. Since 1879 connected with U. S. Geological Survey, Washington, D. C.

Bernays, A. C. 1872-73. M.D. Practicing physician in St. Louis, Mo.

Best, Wm. F. (Fredericton?, N. B.) About 1874-75. Has been analytical chemist in Nova Scotia or New Brunswick.

Blair, Geo. D. (Pittsburg, Pa.) 1870.

\*Blake, Eli W. 1864. At one time professor of chemistry at the University of Vermont, again at Cornell, and later professor of physics at Brown University, Providence, R. I. Died 1895.

Bolton, B. Meade. (Richmond, Va.) 1883-84. M.D., University of Virginia, 1879. Formerly associate at Johns Hopkins, professor in Universities of South Carolina and Missouri; later director of the laboratory of hygiene, board of health, Philadelphia, Pa. Now practicing physician, Princeton, N. J.



- Bolton, H. Carrington. (New York.) 1863-65. Ph.D., Göttingen. Formerly assistant in Columbia School of Mines, professor Woman's Medical College of New York Infirmary, and Trinity College, Hartford, Conn. Present address Cosmos Club, Washington, D. C.
- Borden, Wm. F. (Chicago.) 1868. At one time engaged in metallurgical operations at Leadville, Colo. Present address Borden Block, Randolph and Dearborn Streets, Chicago, Ill.
- \*Bowen, Henry C. About 1875. Instructor in School of Mines, Columbia College, N. Y., and technical chemist. Died 1899.
- Bowman, Walker. 1885. Ph.D., Berlin, 1888. At one time professor of chemistry, Ohio State University, now chemist Louisville Spirit Cured Tobacco Co., Louisville, Ky.
- Boyd, Wm. W. (Boston.) 1872?
- Brewer, Wm. H. (Poughkeepsie, N. Y.) 1855-56. Formerly professor Washington and Jefferson College, Washington, Pa., assistant on Geologic Survey of California, professor University of California. Since 1864 professor of agriculture, Sheffield Scientific School, New Haven, Conn.
- Brown, W. G. 1880-81. Formerly professor Washington and Lee University, Va., chemist Department of Agriculture, Washington, D. C.; now professor University of Missouri, Columbia, Mo.
- Burney, Wm. (Davidson, N. C.) Between 1875-79. Ph.D., 187-. Professor of chemistry, College of South Carolina, Columbia, S. C.
- Burton, Beverly S. 1871. Ph.D., 1871. At one time professor East Tennessee University. Retired from active chemical work. Address Munich, Carlsstr. 61aIII.
- Case, Jos.? Alliene? (Columbia, Pa.?) 1871?
- Caldwell, Geo. C. (Framingham, Mass.) 1857-58. Ph.D., Göttingen 1857. Formerly professor Antioch College, Ohio, and Agricultural College of Pennsylvania. Since 1868 professor agricultural and analytical chemistry, Cornell University, Ithaca, N. Y.
- Chapman, Nelson C. (St. Louis, Mo.) 1870-71. Has not followed chemistry. President Cumberland Construction Co., Chemical Bldg., St. Louis, Mo.
- Chatard, Thos. M. (Baltimore, Md.) 1876. Ph.D., 1876. Formerly chemist U. S. Torpedo Station, Newport, R. I., later U. S. Geological Survey. Not actively engaged in chemistry. Address 1714 Rhode Island Ave., Washington, D. C.
- Comey, Arthur M. (Boston, Mass.) 1884-85. Ph.D., 1885. At one time professor Tufts College, Boston, Mass. Address 54 Concord Ave., Cambridge, Mass.
- Dana, Edward S. (New Haven, Conn.) 1872-73. Ph.D., Yale. Professor Yale University, New Haven, Conn.
- De Fremery, James L. 1885-86. Ph.D., 1886. President and general manager of the American Lucol Co., 44 Broadway, New York City.
- \*Dexter, Wm. Prescott, M.D. (Boston, Mass.) 1855. Died 1890.
- Dodge, Jacob A. (Salem, Mass.) Between 1875-79. Ph.D., 187-. Lately professor of chemistry, University of Minnesota. Present address unknown.
- Doremus, Chas. A. (New York.) 1870-72. Ph.D., 1872. Formerly professor University of Buffalo, N. Y., now assistant professor of chemistry and physics, College of the City of New York.

- Drown, Thos. M. (Philadelphia, Pa.) 1866-68. Formerly professor of chemistry, Lafayette College, Easton, Pa., and Massachusetts Institute of Technology, now president Lehigh University, South Bethlehem, Pa.
- \*Easter, J. D. 1854. Ph.D., 1854. At one time professor of chemistry, University of Georgia, Athens, Ga. Died an Episcopal clergyman in Kentucky.
- Fisher, Davenport. 1854-55. Ph.D., 1854. Analytical chemist, Room 610, Old Insurance Building, Milwaukee, Wis.
- Fisher, Wm. Righter. (Philadelphia, Pa.) 1872. Attorney at law, Stephen Girard Building, Philadelphia, Pa.
- \*Genth, F. A. (Waechtersbach, Hesse-Cassel.) Ph.D., 1846. Received degree at Marburg while Bunsen was professor there; was Bunsen's assistant three years prior to coming to America. Later professor of chemistry and mineralogy, University of Pennsylvania. Died 1893.
- Goodwin, W. L. 1880-81. D.Sc., Edinburgh, 1881. School of Mines, Kingston, Ontario, Canada.
- Goodyear, Henry. (New Haven, Conn.) 1870-71.
- Hague, Arnold. (Boston, Mass.) 1864-65. Assistant Geologist Fortieth Parallel Survey. Since 1879 member U. S. Geological Survey, Washington, D. C.
- Hale, Albert C. (New York.) 1879-80. Ph.D., 1880. Formerly president Colorado State School of Mines. Since 1883 head teacher physical sciences, Boys' High School, Brooklyn, N. Y. Address 551 Putnam Ave.
- \*Hallock, Edward J. 1877-78. Ph.D., 1878. Assistant in chemistry, Columbia University, New York City. Died 1884.
- Hennessy, Walter. 1869-70. Lawyer, 299 Nassau Street, New York City.
- Hilgard, E. W. (Zweibrücken, Rhenish Bavaria.) 1852-53. Ph.D., 1853. Formerly state geologist, and professor of chemistry, University of Mississippi, professor of geology, etc., University of Michigan. Now professor of agriculture, University of California, Berkeley, Cal.
- Hillebrand, Wm. F. (Honolulu, H. I.) 1872-76. Ph.D., 1875. Formerly assayer, Leadville, Colorado. Since 1880, chemist U. S. Geological Survey, Denver, Colorado, and Washington, D. C. Since 1892 also professor of chemistry, National College of Pharmacy, Washington, D. C.
- Hitchcock, H. A. (Chicago.) After 1872.
- Hodges, Harrison B. (Boston, Mass.) 1873-74. Formerly technical chemist in Boston; later with U. P. R. R., Omaha, B. & O. R. R., Baltimore, Southern R. R., Washington, D. C.; now purchasing agent L. I. R. R., Long Island City, N. Y.
- Hodges, N. D. C. 1874-75. Formerly editor "Science"; now librarian Public Library, Cincinnati, Ohio.
- Hunter, Richard. (New York.) 1870.
- \*Irby, Wm. (Virginia.) 1876-77. Ph.D., Bonn.
- Jackson, Chas. Loring. (Boston, Mass.) 1873-74. Professor of chemistry, Harvard University, Cambridge, Mass.
- Jayne, H. W. 1877-78. Ph.D., Strassburg, 1882. Address 931 N. Broad St., Philadelphia, Pa.
- Kinnicutt, Leonard, P. 1875-76. Director chemical laboratory, Worcester Polytechnic Institute, Worcester, Mass.



**Kuntz.** Between 1876-79.

**Lees, Wm. T.** (Brooklyn, N. Y.) 1873-76. Consolidated Gas Company, Avenue A., Corner 21st St., New York City.

**Loeb, Morris.** 1887-88. Professor of chemistry, University of the City of New York.

**Luedeking, Robert.** 1872-73. M.D., 1876, Strassburg. In 1882 lecturer, from 1883-92 incumbent of chair of pathological anatomy, since 1892 of chair of diseases of children in St. Louis Medical College (now a Department of Washington University), St. Louis, Mo.

\***Lupton, N. T.** (Nashville, Tenn.)? 1875. Formerly professor of chemistry, Vanderbilt University, Nashville, Tennessee, later in State University of Alabama. Deceased, Auburn, Ala.

**Magee.** (Philadelphia, Pa.) 1856.

\***McBurney, Henry.** (Boston.) 1864-65. Manufacturing chemist, Boston, Mass.

**McCay, Leroy W.** 1882. Ph.D., Princeton. Professor of chemistry, Princeton University, Princeton, N. J.

**Merrill, N. Fred.** (Charleston, ?.) 1871-72. Professor University of Vermont, Burlington, Vt.

**Michael, Arthur.** 1872-74. Professor of chemistry, Tufts College, Boston, Mass.

**Miller, Geo. M.** (New York.) 1863-65. At one time assistant in assaying, School of Mines, Columbia University, New York. Did not pursue chemistry afterwards.

**Mixer, Wm. G.** (New York.) 1872-73. Professor of chemistry, Sheffield Scientific School, New Haven, Conn.

**Moellman, Rudolph.** (Brooklyn, N. Y.) 1870.

\***Moore, Gideon E.** (New York.) 1870. Ph.D., 1870. Prior to 1867, analytical chemist, San Francisco, and assayer, Virginia City, Nevada. Chemist Passaic Zinc Co., from 1872 to time of death in 1895.

**Mayer, Benj. F.** (New York.) 187-.

**Nichols, Lyman.** (Boston, Mass.) 1863-65. Has not followed chemistry. Address, 14 Commonwealth Ave., Boston, Mass.

**Norton, Sidney A.** (Bloomfield, O.) 1871. Ph.D., Kenyon, 1878. Formerly instructor Cleveland High School, professor of chemistry, Miami University, acting professor of physics, Union College. Since 1873 professor of chemistry, Ohio State University, Columbus, Ohio.

**Norton, Thos. H.** (Rushford, N. Y.) 1873-75. Ph.D. 1875. Formerly manufacturing chemist, Paris, France, professor of chemistry and librarian, University of Cincinnati, Ohio. Now U. S. Consul, Harput, Turkish Armenia.

\***Osburn,** 1874-75. Professor, Wittenberg College, Springfield, Ohio.

**Penny,** 1888. Was instructor in a Methodist College about 1891.

**Pitman, S. Minot.** 1873-74. At one time professor of chemistry, Tufts College, Boston, Mass.; now in insurance business, Providence, R. I.

**Prochazka, Geo. A.** (Newark, N. J.) 1873-74. Ph.D., 1874. Assistant in chemistry, Stevens Institute, Hoboken, N. J.; later analytical and consulting chemist, New York City; since 1881 technical and manufacturing chemist; now president Central Dyestuff and Chemical Co., Plum Point Lane, Newark, N. J. (Address 138 West 13th St., New York.)

- \*Pugh, Evan. (Germantown, Pa.) 1856-57. Ph.D., Göttingen. Formerly president Pennsylvania State College. Died 1864.
- Rau, Henry M. 1877-79. Ph.D., 1879. chemist and chemical manufacturer, 130-132 Pearl St., New York City.
- Reese, Chas. L. (Baltimore, Md.) 1884-86. Ph.D., 1886. Formerly assistant, Johns Hopkins University, professor of chemistry, Wake Forest College, and South Carolina Military College, now chemist, New Jersey Zinc Co., Newark, N. J.
- Reynolds, Geo. (New York.) 1854-55.
- Rising, Willard B. (Mechlenburg, N. Y.) 1869-71. Ph.D., 1871. State analyst and professor of chemistry, University of California, Berkeley, Cal.
- \*Root, Edward Walstein. 1864-65. Formerly assistant in chemistry, Columbia College, School of Mines; then professor of chemistry, Hamilton College, Clinton, N. Y. Died 1870.
- Seely, Henry M. (Onondaga, N. Y.) 1867-68. Formerly professor of chemistry, Berkshire Medical Institute, and Medical Department, University of Vermont; professor of chemistry and natural history, and since 1895, emeritus professor of natural history, Middlebury College, Vermont.
- Slingluff, Frank. (Baltimore, Md.) 1863-65.
- Smith, Eugene Allen. 1866-68. Ph.D., 1868. Prior to 1872 assistant on Geologic Survey of Mississippi, now state geologist and professor of geology and mineralogy, State University of Alabama, University, Alabama.
- Smyth, Geo. A. (Brunswick, .) 1872. Address 120 S. Grove Ave., Oak Park, Ill.
- Soule, Edward. (New Haven, Conn.) 1870.
- Springer, Alfred. 1871-73. Ph.D., 1872. Manufacturing chemist, Cincinnati, Ohio (Box 621).
- Strauss? Fred. (Pittsburg.) 187-.
- Terry, N. W. 1871-72. Ph.D., Göttingen. Professor of physics, U. S. Naval Academy, Annapolis, Md.
- Thomson, Wm. J. (New Orleans.) 187-.
- Treadwell, Fred. P. (Portsmouth, N. H.) 1875-79. Ph.D., 1878. Was Bunsen's lecture assistant for three semesters 1878-79. Ordentlicher professor of chemistry, Eidgenös. Polytechnikum, Zürich, Switzerland.
- Waddell, John. 1883-84. Ph.D., 1884. Professor of chemistry, School of Mines, Kingston, Ontario, Canada.
- Wahl, Wm. H. 1867-68. Ph.D., 1868. Secretary, Franklin Institute, Philadelphia, Pa.
- Waldstein, Martin. (New York.) 1873-75. Ph.D., 1875. Manufacturing chemist, 107 Murray St., New York City.
- \*Walton, Henry C. (New York.) 1870. Died in New York.
- \*Walz, Isidor. (New York.) 1866-68. Ph.D., 1867. Consulting and analytical chemist. Died in New York, 1877.
- \*Webster, . (Pawtucket, R. I.) 1856. Died about 1860 or 1861, shortly after applying for a professorship in Washington and Jefferson College, Washington, Pa.
- Wilkins, Ross. 1879-82. Ph.D., 1882. Has held various positions as

chemist, assayer, and superintendent; now chemist Detroit plant, American Radiator Co., Detroit, Mich.

\*Williams, Geo. H. (Utica, N. Y.) 1880-82. Ph.D., 1882. Professor of inorganic geology, Johns Hopkins University, Baltimore, Md. Died 1894.

Williams, W. J. 1869-70. Chief chemist at the Frankford Arsenal, Philadelphia, Pa.

\*Wolff, Chas. (Cincinnati, Ohio.) 1863-65.

Wolf, Theo. R. 1868-70. Ph.D., 1870. Professor of chemistry, Delaware College, and State Chemist, Newark, Del.

Woodrow, James. 1856.

\*Wright, Harrison. (Wilkesbarre, Pa.) 1869-70. Died 1885.

\* Deceased.





Issued with December Number, 1900.

## Proceedings.

### BOARD OF DIRECTORS.

A meeting of the Board of Directors of the American Chemical Society was held at the Chemists' Club, 108 W. 55th St., New York City, Saturday, October 27, 1900.

The meeting was called to order at 9 o'clock P.M., by President McMurtrie. All the directors were present.

The minutes of all previous meetings were approved as recorded in the secretary's book.

The librarian was authorized to subscribe for the *Berichte* of the German Chemical Society.

It was voted that the president appoint a committee of two directors to whom should be referred the manuscript of the index prepared by Mr. Sohon, and the galley proof thus far prepared, and who shall examine into the question of errors submitted by the editor and report the same to the Board at its next meeting. Messrs. E. E. Smith and C. A. Doremus were appointed such committee.

The treasurer of the society was empowered to pay the necessary expenses for inserting funeral notices of the late Dr. E. R. Squibb in the daily papers.

The minutes of the meeting were read and approved and the meeting then adjourned.

ALBERT C. HALE, *Secretary*.

### COUNCIL.

A local section of the Society for the benefit of those members who reside in and around Kansas City, Mo., to embrace those portions of the States of Missouri and Kansas included between the 93rd and 98th meridians, with headquarters at Kansas City,

Mo. (714 Wyandotte St.), was authorized by the Council, November 6.

#### NAMES PROPOSED FOR MEMBERSHIP.

Boesch, Basil W., 36 Union Park, Boston, Mass.  
 Brown, C. Arthur, 630 W. 8th St., Cincinnati, Ohio.  
 Burt, Stratford, 840 Halsey St., Brooklyn, N. Y.  
 Caspari, Chas. E., 312 W. 115th St., N. Y. City.  
 Cathcart, Wm. K., Maywood, N. J.  
 Chambliss, Hardee, 312 W. 115th St., N. Y. City.  
 Cook, Alfred N., Sioux City, Iowa.  
 Davis, Leon K., 185 Temple St., West Newton, Mass.  
 Dodge, Francis D., 60 S. Oxford St., Brooklyn, N. Y.  
 Dreyfus, Wolfram E., 175 W. 107th St., N. Y. City.  
 Henius, Max, 290 S. Water St., Chicago, Ill.  
 Hummell, A. S., Box 195, High Bridge, N. J.  
 Hunter, Edwin E., 122 S. 3rd St., St. Joseph, Mo.  
 Jordan, James O., 994 Washington St., Boston, Mass.  
 Josephson, Edgar, 131 Amity St., Brooklyn, N. Y.  
 Kingman, Wm. A., 55 Lincoln St., So. Framingham, Mass.  
 Laws, Eugene H., 54 Kellogg St., Fall River, Mass.  
 Mead, George H., Cellulose Products Co., Boston, Mass.  
 Morgan, Leonard P., 4714 Chester Ave., Philadelphia, Pa.  
 Owens, Wm. G., Bucknell Lab., Lewisburg, Pa.  
 Patterson, G. W., Indian Head, Md.  
 Roberts, Alfred E., 23 St. Botolph St., Boston, Mass.  
 Robison, F. W., Columbus Ford Lab., 103 State St., Chicago, Ill.  
 Shepherd, Earnest S., Remington, Ind.  
 Sinkinson, Joseph D., 85 Willow St., Brooklyn, N. Y.  
 Sparks, John C., Bement Ave., Livingston, Richmond Co., N. Y.  
 Stieglitz, Julius, Univ. of Chicago, Chicago, Ill.  
 Tingle, Alfred, Chem. Lab., Columbia Univ., N. Y. City.  
 Tingle, John B., Lewis Inst., Chicago, Ill.  
 Tolman, Lucius M., 1937 13th St., N.W., Washington, D. C.  
 Trowbridge, Dic. H., Lewis Inst., Chicago, Ill.  
 Waterhouse, James S., Cumberland Univ., Lebanon, Tenn.  
 Wahl, Dr. Robert, 290 S. Water St., Chicago, Ill.  
 Waters, Charles D., 6 Magnolia St., Roxbury, Mass.  
 Waters, C. E., Conn. Agr. Coll., Storrs, Conn.  
 Wesener, John A., Columbus Ford Lab., 103 State St., Chicago, Ill.  
 Ulmer, George F., Arbuckle Bros., Sugar Ref., Foot of Pearl St., Brooklyn, N. Y.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Bernheim, Geo. B., 74 E. 79th St., N. Y. City.  
 Hellon, Robert, 40 Lowther St., Whitehaven, Eng.  
 Hildreth, Thomas F., 530 W. 123rd St., N. Y. City.  
 Kaufman, G. Falk, 63 E. 74th St., N. Y. City.  
 Lindsay, William G., 207 W. 81st St., N. Y. City.  
 Moffatt, Miles R., Momaroneck, Westchester Co., N. Y.  
 Page, Robert W., 527 Third St., Brooklyn, N. Y.  
 Pickhardt, W. Paul, 1042 Madison Ave., N. Y. City.

ASSOCIATES ELECTED OCT. 12, 1900.

Braun, F. W., 501-505 N. Main St., Los Angeles, Cal.  
 Hicks, Walter T., 300 S. Broadway, N. Y. City.  
 Baxter, W. T., Rolla, Mo.

NEW MEMBERS ELECTED OCT. 12, 1900.

Johnson, Charles M., 701 Orchard St., Avalon, Pa.  
 Rademacher, Hermann A., Box 243, Lawrence, Mass.  
 Rogers, Herbert F., Provident Chem. Wks., St. Louis, Mo.  
 Vosburgh, C. H., High School, Jamaica, N. Y.

NEW MEMBERS ELECTED NOVEMBER 19, 1900.

Balcom, Reuben W., Mass. Inst. Tech., Boston, Mass.  
 Baltzly, Edwin B., Perth Amboy, N. J.  
 Benedict, Francis G., Middletown, Conn.  
 Braman, Winfred W., Durham, N. H.  
 Breves, Rudolph, Rahway, N. J.  
 Brown, John W., 126 Massachusetts Ave., Boston, Mass.  
 Champion, E. C., Iola Portland Cement Co., Iola, Kans.  
 Gordon, A. S., Oliver Iron Mining Co., Mountain Iron, St. Louis Co., Minn.  
 Grainger, William E., Cranberry, Mitchell Co., N. C.  
 Hemmings, Frederick J., 12 Pearl St., Boston, Mass.  
 Heckeroth, William C., 3443 N. 18th St., Philadelphia.  
 Heckman, J. Conrad, Larkin Soap Co., Buffalo, N. Y.  
 Melcher, Arthur C., 58 Bowen St., Newton Centre, Mass.  
 Morgan, W. C., Washburn College, Topeka, Kans.  
 Osgyani, Arpad, 64 Orchard St., Astoria, L. I., N. Y.  
 Pough, Francis H., 146 Hicks St., Brooklyn, N. Y.  
 Walton, James H., Jr., Room 317, 126 Massachusetts Ave., Boston, Mass.  
 Wheeler, Alwyn S., Chapel Hill, N. C.  
 Woods, Chas. D., Orono, Me.

ASSOCIATES ELECTED NOVEMBER 19, 1900.

Cary, Edward A., Lafayette College, Easton, Pa.  
 Felt, W. W., 9431 Normal Ave., Chicago.

Haskell, Albert A., Essex, Mass.

Howard, John J., 118 McKeen Hall, Easton, Pa.

#### CHANGES OF ADDRESS.

Belden, A. W., Tenn. C. I. and R. Co., Birmingham, Ala.

Bigelow, S. Lawrence, 1520 Hill St., Ann Arbor, Mich.

Blouin, R. E., care Sugar Planters' Expt. Sta., Honolulu, Hawaiian Territory.

Chamberlin, W. E., 111 Water St., N. Y. City.

Cornelison, R. W., Bloomfield, N. J.

Corse, Wm., 26 Hendrie Ave., Detroit Mich.

Falkenau, L., 538 Sacramento St., San Francisco, Cal.

Fay, Irving W., 177 Woodruff Ave., Brooklyn, N. Y.

Fourneaux, E. A., 130 W. 84th St., N. Y. City.

Gallagher, Phil. C., care Boston Gold Copper Sm. Co., Leadville, Colo.

Gallivan, F. B., 56 Prospect Place, Brooklyn, N. Y.

Granja, Rafael, Box 799, Kingston, R. I.

Gudeman, Edward, 4319 Vincennes Ave., Chicago, Ill.

Harding, Everhart P., Univ. of Minnesota, Minneapolis, Minn.

Harrison, J. B., care Harrison, Griffin & Co., Bridgewater Place, Manchester, Eng.

Hart, Edwin B., care Frau Rothchild, 11 Steinweg, Marburg, Germany.

Hinds, J. I. D., Univ. of Nashville, Nashville, Tenn.

Hopkins, Erastus, Lake Mary, Fla.

Jacobs, Chas. B., 44 Broad St., N. Y. City.

Keller, Edward, Box 724, Baltimore, Md.

Kendall, Arthur I., care Cinclare Cent. Factory, Cinclare, La.

Knight, Geo. W., 39 Front St., Schenectady, N. Y.

Kohr, D. A., 110 Huntington Ave., Boston, Mass.

Lazell, E. W., 1130 Walnut St., Philadelphia, Pa.

Logan, Miss Lily, Majestic Hotel, 72nd St. and 8th Ave., N. Y. City.

Lyng, M. H., Union Bag & Paper Co., Sandy Hill, N. Y.

Miller, S. C., 929 New York Ave., N. W., Washington, D. C.

Mommers, Richard, care Glucose Sugar Ref. Co., Marshalltown, Iowa.

Neilson, Thos., Silver Bell Camp., Redrock, Pinal Co., Ariz.

Neish, Arthur C., Columbia Univ., N. Y. City.

Nelson, E. K., 4220 Grand Boulevard, Chicago, Ill.

Parker, Francis L., Jr., Johns Hopkins Univ., Baltimore, Md.

du Pont, Pierre S., Lorain, Ohio.

Redpath, Leon W., 22 Catherine St., Newport, R. I.

Reuter, L. H., Rue de Mérode 17, Brussels, Belgium.

Rickards, Burt R., 607 Sudbury Bldg., Boston, Mass.



Riggs, G. W. 46 E. 29th St., N. Y. City.  
 Rogers, Allen, 3605 Locust St., Phila., Pa.  
 Saarbach, Ludwig, 114 Pearl St., N. Y. City.  
 Sadtler, S. P., N. E. Cor. 10th and Chestnut Sts., Philadelphia, Pa.  
 Sargent, Chas. L., Murphy Varnish Co., Newark, N. J.  
 Schuyler, E. H., Erie High School, Erie, Pa.  
 Sherrard, V. P., Bland, N. M.  
 Shilstone, H. M., Miles' Planting & Mfg. Co., Burnside, La.  
 Thompson, Firman, Bundaberg, Queensland, Australia.  
 Van Gelder, A. P., Landing, N. J.  
 Walker, Claude F., New Britain, Conn.  
 Watson, E. T., 172 E. Main St., Chillicothe, Ohio.  
 Willcox, F. A., The Oaks, West, Sunderland, Eng.  
 Woolworth, James G., 11 Halsey St., Providence, R. I.

#### ADDRESS WANTED.

Emmens, Stephen H., formerly of 1 Broadway, N. Y. City.

### MEETINGS OF THE SECTIONS.

#### NORTH CAROLINA SECTION.

The Fall meeting of the section was called to order in Crowell Science Hall, Trinity College, Durham, by the presiding officer, Prof. B. W. Kilgore, on November 9, 1900, at 8 P.M. Thirty members and visitors were present. The following papers were read and discussed:

"International Atomic Weights," by Charles Baskerville.

"The Soil Survey in North Carolina and the Practical Value of the Results," by C. D. Harris.

"Notes on the Adie and Wood Method for the Determination of Potassium," by Charles Baskerville and I. F. Harris.

"The Determination of Certain Organic Radicals," by Charles E. Brewer.

"Formaldehyde as a Preservative of Food Material and its Detection," by W. M. Allen.

"Richter and the Periodic Law," by F. P. Venable.

"The Basis of Scientific Thought," by Charles Baskerville.

"Kilgore's Modification of the Volumetric Method of Estimating Phosphoric Acid," by C. B. Williams.

Reduction Products of Dehydromucic Acid," by H. B. Hill and A. S. Wheeler.

"The Oxidation of Cellulose," by A. S. Wheeler.

"The Necessity for State Supervision of Escaping Noxious Vapors and Contamination of Streams from Manufacturing Enterprises," by Charles Baskerville.

"Some New Chromium Salts," by J. E. Mills.

"Exhibition of a Mechanism for Marking Calibrated Apparatus," by C. B. Williams.

"Individual Effort as a Factor in Organized Scientific Work," by B. W. Kilgore.

There being no further business the section adjourned.

C. B. WILLIAMS, *Secretary*.

#### NEW YORK SECTION.

The October meeting was held on the 5th at the Chemists' Club. The papers read were:

"Dr. Meyers' Tangent System of Sulphuric Acid Manufacture," by C. Glaser.

"Note on the Determination of Zinc in the Franklin, New Jersey, Ores by the Ferrocyanide Method," by William H. Bassett.

The Chair appointed the following Committee on Prizes: C. Richardson, P. de P. Ricketts, and M. Loeb.

M. T. BOGERT, *Secretary pro tem*.

The November meeting was held on Friday evening, November 9th, at the Chemists' Club.

The minutes of the previous meeting were read and approved.

A paper entitled "A Brief Review of Antipyrin and Its More Important Derivatives," was read by D. C. Eccles.

A motion was made to appoint a Committee on Papers. It was seconded and carried.

A motion to elect a vice-chairman was made and seconded, and the election proceeded with. M. T. Bogert was unanimously elected.

A motion to publish an annual report was lost.

The death of Dr. E. R. Squibb was formally announced and a brief sketch of his life by Dr. Charles Rice, was read by the chairman.

It was voted to appoint a committee to draft suitable resolutions expressing the Society's appreciation of Dr. Squibb's

character, of his services to chemical science, and of the loss sustained by his death; and that the said resolutions be engrossed in duplicate, a copy to be sent to his family and one to be preserved by the Society.

The meeting was then adjourned.

DURAND WOODMAN, *Secretary*.

#### LEHIGH VALLEY SECTION.

A regular meeting of the Lehigh Valley Section was held at South Bethlehem, in the chemical laboratory of Lehigh University, on Thursday evening, October 18th. Resolutions were adopted relative to the establishment of a National Standards Bureau and of a Bureau of Chemistry in the United States Department of Agriculture to prevent the adulteration, etc., of food, after which the following papers were read:

“A Water-jacketed Crucible,” by Dr. Porter W. Shimer; “Rapid Estimation of Sulfur in Iron,” by Dr. Porter W. Shimer; “Valuation of Iron in Magnetite Ore by Specific Gravity Test,” by Dr. Joseph W. Richards; and “A Method for Preparing Exactly Normal, Seminormal, Decinormal, etc., Sulfuric Acid,” by Richard K. Meade.

The papers were discussed by Drs. Shimer, Richards, and Von Wachtel. In addition to the above, Dr. Richards who had just returned from Paris, entertained the section with a short interesting talk on the metallurgical exhibits at the Exposition.

RICHARD K. MEADE, *Secretary*.



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OF THE

# American Chemical Society.



SEPTEMBER, 1900.





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SEPTEMBER, 1900.

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- \*WHEELER, FRIEDRICH, Göttingen, Germany.

\* Deceased.

# MEMBERS.

## FOR THE YEAR 1900.

*Names of life members are printed in heavy capitals.*

- \*1898 **ABEL**, John J ..... 1604 Bolton St., Baltimore, Md.  
 1900 Ackerman, Franz W ..... Box 487, Far Rockaway, Long Island,  
 N. Y.  
 1876 Adams, Isaac ..... 1776 Massachusetts Ave., N. Cambridge,  
 Mass.  
 1898 Adams, Maxwell ..... 5815 Drexel Ave., Chicago, Ill.  
 1900 Adams, Walter O ..... 1776 Massachusetts Ave., N. Cambridge,  
 Mass.  
 1895 Adgate, Matthew ..... Care of General Chemical Co., Syracuse  
 Works, Syracuse, N. Y.  
 1889 Adriance, John S ..... 105 E. 39th St., N. Y. City.  
 1897 Affelder, Oscar I ..... Care of Pittsburg Gas and Coke Co., Otto,  
 Pa.  
 1896 Alden, John ..... Lawrence, Mass.  
 1897 Alexander, Jerome ..... Care of Nat. Gum and Mica Co., 502-510  
 W. 45th St., N. Y. City.  
 1898 Allen, Charles M ..... Pratt Institute, Brooklyn, N. Y.  
 1898 Allen, Chas. R ..... New Bedford High School, New Bedford,  
 Mass.  
 1894 Allen, E. W ..... 1725 Riggs Pl., Washington, D. C.  
 1900 Allen, Richard F ..... Hart Park, West New Brighton, Staten  
 Island, N. Y.  
 1893 Allen, Walter S ..... 34 So. 6th St., New Bedford, Mass.  
 1899 Aller, F. D ..... Maurer, N. J.  
 1897 Alsop, William K ..... 30 Ferry St., N. Y. City.  
 1899 Alway, F. J ..... Chem. Dept., Neb. Wesleyan Univ., Uni-  
 versity Place, Neb.  
 1876 Amend, B. G ..... 205 3d Ave., N. Y. City.  
 1890 Amend, Otto P ..... Care of Eimer & Amend, 3d Ave. and  
 18th St., N. Y. City.  
 1897 Anderson, Duncan, Jr ..... 104 8th Ave., Roanoke, Va.  
 1892 Andrews, Frank H ..... Box 476, Providence, R. I.  
 1893 Andrews, George F ..... Care of Cornell & Andrews, Providence,  
 R. I.  
 1892 Andrews, Launcelot W ..... State Univ. of Iowa, Iowa City, Ia.

\* The column of dates at the left hand of the page gives the date of admission of each member to the Society. Members and associates will confer a favor by informing the secretary of any error in name, address, or date of admission.

- 1896 Andrews, W. W.....Mt. Allison College, Sackville, N. B.  
1900 Ansbacher, Louis A .....4 Murray St., N. Y. City.  
1894 Appleby, Wm. R.....911 S. E. 5th St., Minneapolis, Minn.  
1877 Appleton, John Howard .....Brown Univ., Providence, R. I.  
1900 Archibald, Eben H.....Harmony, Colchester Co., N. S.  
1900 Armsby, H. P.....State College, Pa.  
1898 Armstrong, Henry E.....Central Technical College, Exhibition  
Road, London, S. W., England.  
1896 Arnold, Fred. N., Jr.....Care of The N. K. Fairbank Co., St.  
Louis, Mo.  
1900 Arnott, Geo. W. Campbell ..26 Broadway, N. Y. City.  
1896 Asbury, S. E.....Dept. of Agr., Raleigh, N. C.  
1899 Ashley, Harrison E .....947 Acushnet Ave., New Bedford, Mass.  
1899 Atkinson, Elizabeth A.....4109 Locust St., Philadelphia, Pa.  
1899 Atkinson, J. W .....Santa Maria, Cal.  
1897 Attix, James C.....873 N. 24th St., Philadelphia, Pa.  
1893 Atwater, R. M.....Solvay Process Co., Syracuse, N. Y.  
1893 Atwater, Wilbur O.....Wesleyan Univ., Middletown, Conn.  
1892 Atwood, Frank W .....Care of T. L. Mayo & Co., 98 Commercial  
St., Boston, Mass.  
1898 Atwood, Wm. P .....11 Harding St., Lowell, Mass.  
1898 Aubert, A. B.....Univ. of Maine, Orono, Me.  
1894 Auchy, George.....6948 Hegerman St., Tacony, Philadel-  
phia, Pa.  
1890 Austen, Peter T.....52 Beaver St., N. Y. City.  
1899 Austin, Ned M.....1236 Pennsylvania Ave., Allegheny, Pa.  
1895 Avery, Samuel.....Univ. of Idaho, Moscow, Ida.  
1894 Axtell, Frank C.....Box 116, Short Hills, N. J.  
1899 Aylsworth, J. W .....223 Midland Ave., East Orange, N. J.  
1898 BABB, F. E.....61 Myrtle St., Boston, Mass.  
1900 Bach, August .....537 Nelson St., Chicago, Ill.  
1892 Baekeland, Leo .....Care of Nepera Chem. Co., Nepera Park,  
N. Y.  
1898 Baer, S. H.....158 Chambers St., N. Y. City.  
1893 Bailey, E. H. S .....Univ. of Kansas, Lawrence, Kans.  
1895 Bailey, Ralph W .....1165 E. Jersey St., Elizabeth, N. J.  
1891 Baird, J. W .....Mass. College of Pharmacy, Boston, Mass.  
1893 Baker, Haydn M.....27 Hart St., Brooklyn, N. Y.  
1894 Baker, John T .....Easton, Pa.  
1894 Baker, Philip S .....De Pauw University, Greencastle, Ind.  
1896 Baker, Theodore .....Box 116, Pompton Lakes, N. J.  
1900 Baldwin, Charles E .....197 Auburn St., Cambridgeport, Mass.  
1889 Baldwin, Herbert B .....906 Broad St., Newark, N. J.  
1899 Bancroft, Wilder D.....7 East Ave., Ithaca, N. Y.  
1899 Banghart, Edgar D.....Crete, Nebr.

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|------|----------------------------|--|
| 1894 | Bannan, John F.....        | North Andover, Mass.   |
| 1898 | Bardwell, Fred. L.....     | Mass. Inst. Tech., Boston, Mass.                                     |
| 1898 | Baringer, F. J .....       | Care of Wm. S. Merrell Chem. Co., Cin-<br>cinnati, O.                |
| 1890 | Barker, George F .....     | 3909 Locust St., Philadelphia, Pa.                                   |
| 1898 | Barlow, W. H .....         | Pasadena, Cal.   |
| 1900 | Barnes, Bayard.....        | Sheffield Chem. Lab., New Haven, Conn.                               |
| 1899 | Barnett, Edwin S.....      | Mt. Alverno, Delaware Co., Pa.                                       |
| 1896 | Barrett, Jesse M.....      | 908 S. 5th St., East, Cedar Rapids, Iowa.                            |
| 1895 | Barrows, W. A., Jr.....    | Care of Mahoning Valley Iron Co.,<br>Youngstown, O.                  |
| 1895 | Bartlett, E. J .....       | Dartmouth College, Hanover, N. H.                                    |
| 1885 | Bartley, E. H.....         | 21 Lafayette Ave., Brooklyn, N. Y.                                   |
| 1891 | Barton, G. E.....          | Care of Whitall, Tatum & Co., Flint Glass<br>Works, Millville, N. J. |
| 1896 | Bartow, Edward .....       | Univ. of Kansas, Lawrence, Kans.                                     |
| 1894 | Baskerville, Chas.....     | Univ. of N. C., Chapel Hill, N. C.                                   |
| 1898 | Bassett, George O.....     | 30 Farnsworth St., South Boston, Mass.                               |
| 1898 | Bassett, Wm. H.....        | N. J. Zinc Co., Newark, N. J.  |
| 1898 | Bates, H. R.....           | North Weymouth, Mass.  |
| 1898 | Bauer, Wm. C .....         | Baker Univ., Baldwin, Kans.  |
| 1876 | Baumgarten, F. M .....     | 485 Marshall St., Milwaukee, Wis.                                    |
| 1898 | Baxter, Gregory P .....    | Haverford Coll., Haverford, Pa.                                      |
| 1899 | Baxter, William T .....    | 254 New York St., Aurora, Ill.                                       |
| 1898 | Beach, Irving E.....       | Lawrence, Mass.  |
| 1895 | Beal, J. H .....           | Scio College, Scio, Ohio.  |
| 1897 | Beal, W. H .....           | Dept. of Agr., Washington, D. C.                                     |
| 1900 | Beans, Hal T.....          | Univ of Nebr., Lincoln, Nebr.  |
| 1895 | Becher, Jesse B.....       | 1104 Douglass St., Sioux City, Iowa.                                 |
| 1898 | Beck, Herbert H.....       | 105 A Queen St., Lancaster, Pa.                                      |
| 1898 | Beck, Oscar C .....        | 470 Second St., Brooklyn, N. Y.                                      |
| 1893 | Becnel, Lézin A.....       | Luling P. O., La.  |
| 1895 | Beeson, Jasper L.....      | Ga. Nor. and Indus. Coll., Milledgeville,<br>Ga.                     |
| 1876 | Behr, Arno .....           | Arlington Court, Pasadena, Cal.                                      |
| 1900 | Behr, Gustave E., Jr ..... | Harvard Univ., Cambridge, Mass.                                      |
| 1896 | Belden, A. W .....         | Birmingham Cement Co., Eusley, Ala.                                  |
| 1896 | Bellam, Henry L.....       | Box 271, Anaconda, Mont.   |
| 1893 | Benjamin, Marcus .....     | U. S. National Museum, Washington,<br>D. C.                          |
| 1891 | Bennett, A. A.....         | Iowa State College, Ames, Iowa.                                      |
| 1898 | Bennett, Frank W .....     | 13 Broad St., Boston, Mass.  |
| 1898 | Benson, David H.....       | Box 96, North Weymouth, Mass.  |
| 1894 | Benton, Geo. W.....        | 525 N. Pennsylvania St., Indianapolis,<br>Ind.                       |

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|------|------------------------|---|
| 1900 | Benton, S. Irving      | 249 E. Logan Sq., Philadelphia, Pa.                                       |
| 1894 | Berghausen, E. J       | 644 Crown St., Cincinnati, O.   |
| 1900 | Berkeley, Wm. N        | Box 65, San Juan, Puerto Rico.  |
| 1900 | Bernhard, Adolph       | Univ. of Chicago, Chicago, Ill.   |
| 1891 | Berry, W. G            | 329 W. 83rd St., N. Y. City.  |
| 1900 | Bertelli, Riccardo     | 20 W. 16th St., N. Y. City.   |
| 1896 | Best, Otto             | Bay and Dupont Sts., San Francisco, Cal.                                  |
| 1898 | Betts, Anson G         | Lansingburg, N. Y.  |
| 1897 | Bevier, Isabel         | Univ. of Illinois, Champaign, Ill.  |
| 1899 | Bigelow, S. Lawrence   | 321 S. Division St., Ann Arbor, Mich.                                     |
| 1893 | Bigelow, W. D.         | Dept. of Agr., Washington, D. C.  |
| 1895 | Billings, E. F.        | 144 High St., Boston, Mass.   |
| 1894 | Bird, Herbert S.       | Care of N. Y. Tartar Co., 9th St. and<br>Gowanus Canal, Brooklyn, N. Y.   |
| 1899 | Bird, Maurice          | Calhoun, La.  |
| 1896 | Bischoff, Ernst        | 87-89 Park Place, N. Y. City.   |
| 1895 | Bizzell, James A.      | W. Raleigh, N. C.   |
| 1900 | Black, Otis F          | 10 Avon St., Cambridge, Mass.   |
| 1898 | Blackmore, Henry S     | 206 S. 9th Ave., Mount Vernon, N. Y.                                      |
| 1899 | Blackshear, Charles C. | The Woman's College, Baltimore, Md.                                       |
| 1897 | Blair, A. W.           | Box 196, Lake City, Fla.  |
| 1894 | Blair, Andrew A        | 406 Locust St., Philadelphia.   |
| 1900 | Blake, Lucien I        | Univ. of Kansas, Lawrence, Kas.   |
| 1898 | Blanchard, Arthur A    | Mass. Inst. Tech., Boston, Mass.  |
| 1895 | Blasdale, W. C.        | 2614 Channing Way, Berkeley, Cal.   |
| 1893 | Bloomfield, Lloyd M    | Marlboro, Stark Co., O.   |
| 1893 | Blouin, R. E.          | Audubon Park, New Orleans, La.  |
| 1895 | Bogardus, C. E         | 60 Columbia St., Seattle, Wash.   |
| 1894 | Bogert, Marston T      | Havemeyer Hall, Columbia Univ., Boule-<br>vard and 116th St., N. Y. City. |
| 1900 | Boggs, Gilbert H       | 603 S. 42nd St., Philadelphia.  |
| 1895 | Böhm, L. K             | 320 Broadway, N. Y. City.   |
| 1900 | Bolling, Randolph      | Care Va. I. C. and C. Co., Buena Vista<br>Furnace, Buena Vista, Va.       |
| 1891 | Bolton, H. Carrington  | Cosmos Club, Washington, D. C.  |
| 1900 | Boltwood, Bertram B.   | Sheffield Scientific School, New Haven,<br>Conn.                          |
| 1900 | Bonnet, Frederic, Jr.  | 13 Mellen St., Cambridge, Mass.   |
| 1896 | Bookman, Samuel        | 9 E. 62nd St., N. Y. City.  |
| 1880 | Booraem, J. V. V       | 204 Lincoln Pl., Brooklyn, N. Y.  |
| 1896 | Boot, J. C             | Klatten, Java, Dutch East Indies.   |
| 1896 | Borland, Charles R     | Care "E. C." and "Schultze" Powder<br>Co., Oakland, Bergen Co., N. J.     |
| 1900 | Boroschek, Leopold     | 149 E. 56th St., N. Y. City.  |
| 1899 | Bosart, Louis W., Jr   | Home City, Hamilton Co., O.   |
| 1893 | Bouton, Rosa           | Chem. Dept., State Univ., Lincoln, Neb.                                   |

- 1897 Bower, W. H ..... 29th St. and Gray's Ferry Road, Philadelphia, Pa.
- 1896 Bowman, J. W ..... 54 S. Huron St., Wheeling, W. Va.
- 1891 Bowman, Walker ..... Lynchburg, Va.
- 1894 Boyer, Charles S ..... Camden, N. J.
- 1891 Boynton, C. Smith ..... 69 N. Prospect St., Burlington, Vt.
- 1894 Brackett, R. N ..... Box 13, Clemson College, S. C.
- 1899 Bradbury, Robert H ..... Central M. T. School, Philadelphia, Pa.
- 1898 Bradford, Ernest ..... Ohio State Univ., Columbus, O.
- 1899 Bradley, Walter P ..... 242 High St., Middletown, Conn.
- 1898 Bragg, Charlotte A ..... Wellesley College, Wellesley, Mass.
- 1880 Bragg, E. B ..... 242 Kennard St., Cleveland, O.
- 1896 Brakes, James ..... Care Chateaugay Ore and Iron Co., Lyon Mountain, N. Y.
- 1900 Breer, Louis ..... Builders Iron Foundry, Providence, R. I.
- 1899 Bregowsky, Ivan M ..... Société Anonyme Westinghouse, 2 Prilukskaya, St Petersburg. Russia.
- 1883 Breneman, A. A ..... 97 Water St., N. Y. City.
- 1890 Brewer, C. E ..... Wake Forest, N. C.
- 1899 Brewster, Edward E ..... 316 East C St., Iron Mountain, Mich.
- 1892 Breyer, Theodor ..... P. O. Box 112, Peoria, Ill.
- 1892 Briggs, T. L ..... Box 533, Ridgewood, N. J.
- 1893 Brinker, Harry L ..... 530 Covington St., Youngstown, O.
- 1895 Broadhurst, W. Homer ..... 13-21 Park Row, N. Y. City.
- 1899 Brown, H. E ..... 107 Marshall St., Coldwater, Mich.
- 1893 Brown, H. F ..... U. S. Naval Torpedo Station, Newport, R. I.
- 1894 Brown, Lucius P ..... 150 N. Cherry St., Nashville, Tenn.
- 1896 Brown, Thomas, Jr ..... La Gran Fundicion Central Mexicana, Aguascalientes, Mexico.
- 1900 Brown, Walter B ..... Care of Nelson Morris & Co., U. S. Yards, Chicago, Ill.
- 1877 Brown, W. G ..... Univ. of Mo., Columbia, Mo.
- 1894 Browne, Arthur L ..... Baltimore Medical College, Baltimore, Md.
- 1898 Browne, Charles A., Jr ..... Univ. of Göttingen, Göttingen, Germany.
- 1897 Browning, Philip E ..... Kent Chem. Lab., Yale Univ., New Haven, Conn.
- 1893 Bruckmann, Gustav T ..... 192 18th St., Brooklyn, N. Y.
- 1899 Brush, Charles F ..... 1003 Euclid Ave., Cleveland, O.
- 1898 Bucher, John E ..... R. I. Coll. A. and M. Arts, Kingston, R. I.
- 1894 Buck, C. Austin ..... Bethlehem Steel Co., So. Bethlehem, Pa.
- 1898 Buffington, Elisha L ..... 33 Chestnut St., Worcester, Mass.
- 1900 Bullard, Frank D ..... 245 Bradbury Block, Los Angeles, Cal.
- 1897 Burk, W. E ..... Male High School, Louisville, Ky.

- 1894 Burleigh, Wm. F .....Care of West Bergen Steel Works, Jersey City, N. J.
- 1897 Burn, Harry .....Sloss-Sheffield S. and I. Co., Birmingham, Ala.
- 1898 Burnside, Charles F.....Int. Sm. Powder and Dynamite Co., South Amboy, N. J.
- 1894 Burr, E. C.....1722 Vallejo St., San Francisco, Cal.
- 1894 Burrell, Loomis.....Care of D. H. Burrell and Co., Little Falls, N. Y.
- 1895 Burt, M. C.....Penna. Mil. Coll., Chester, Pa.
- 1894 Burwell, Arthur W.....208 Superior St., Cleveland, O.
- 1898 Busby, Fred. E.....Adams, Mass.
- 1892 Bush, Charles S.....212 Weybosset St., Providence, R. I.
- 1900 Button, Ok.....Box 233, Trenton, Mich.
- 1892 Byrnes, Eugene A.....U. S. Patent Office, Washington, D. C.
- 1899 CADY, Walter B .....Expt. Station, Columbia, Mo.
- 1899 Cairns, Fred. I.....Anaconda, Mont.
- 1890 Caldwell, G. C.....Cornell Univ., Ithaca, N. Y.
- 1896 Caldwell, Thomas O.....Virginia City, Mont.
- 1893 Calkin, W. S.....Spring Forge, Pa.
- 1898 Calvert, Sidney .....State Univ., Columbia, Mo.
- 1895 Cameron, Frank K .....Cosmos Club, Washington, D. C.
- 1893 Camp, J. M.....Duquesne Steel Works, Duquesne, Pa.
- 1899 Campbell, Archibald .....3140 Duwell Ave., Walnut Hills, Cincinnati, O.
- 1892 Campbell, Edward D.....1310 Hill St., Ann Arbor, Mich.
- 1894 Campbell, George F.....82 Broadway, New Haven, Conn.
- 1896 Cappon, Thomas W.....688 E. 139th St., N. Y. City.
- 1899 Carel, Herbert C .....College of Medicine, Univ. of Minnesota, Minneapolis, Minn.
- 1895 Carlsson, Hugo .....Dominion Iron and Steel Co., Sydney, Cape Breton, N. S.
- 1895 Carman, John S.....472 2nd Ave., Detroit, Mich.
- 1895 Carmichael, Henry.....12 Pearl St., Boston, Mass.
- 1895 Carnell, Wm. C.....Care of Nelson Morris & Co., U. S. Yards, Chicago, Ill.
- 1898 Carpenter, F. B.....Va.-Ca. Chemical Co., Richmond, Va.
- 1894 Carpenter, Thomas B .....142 N. Pearl St., Buffalo, N. Y.
- 1899 Carr, Louis B.....Ouray, Colo.
- 1898 Carr, Robert F.....145 Van Buren St., Chicago, Ill.
- 1900 Carveth, Hector R .....Chem. Lab., Cornell Univ., Ithaca, N. Y.
- 1898 Casamajor, Walter .....372 Greene Ave., Brooklyn, N. Y.
- 1896 Case, Wm. A .....412 E. Randall St., Baltimore, Md.
- 1894 Cathcart, Charles S .....New Brunswick, N. J.
- 1890 Catlin, Charles A .....133 Hope St., Providence, R. I.

- 1886 Cawley, John .....278 Passaic St., Newark, N. J.  
1899 Cayvan, Llewellyn L.....499 Adams St., Chicago, Ill.  
1899 Chace, Edward MacKay.....Berwyn, Md.  
1898 Chalon, P F .....86 Rue Cardinet 86, Paris, France.  
1898 Chamberlain, George E .....Glucose Works, Beach and Taylor Sts.,  
Chicago, Ill.  
1899 Chamberlain, Joseph S .....Oberlin College, Oberlin, O.  
1896 Chamberlin, W. E .....127 Pearl St., N. Y. City.  
1896 Chamot, E. M .....Cornell Univ., Ithaca, N. Y.  
1876 CHANDLER, C. F .....Columbia Univ., N. Y. City.  
1894 Chandler, Wm. H.....South Bethlehem, Pa.  
1898 Chapin, L. Paul.....Mass. Inst. Tech., Boston, Mass.  
1894 Chapman, D. W .....352 23d St., Chicago, Ill.  
1900 Chase, March F.....Mineral Point Zinc Co., Mineral Point,  
Wis.  
1893 Chatard, Thomas M.....1714 Rhode Island Ave., Washington,  
D. C.  
1895 Chauvenet, W. M.....620 Chestnut St., St. Louis, Mo.  
1891 Chazal, P. E.....Box 284, Charleston, S. C.  
1896 Cheney, John P.....So. Manchester, Conn.  
1895 Chesnut, Victor King .....Biochemic Lab., Dept. of Agr., Washing-  
ton, D. C.  
1876 Chester, Albert H .....39 College Ave., New Brunswick, N. J.  
1898 Chittenden, Russell H.....Yale Univ., New Haven, Conn.  
1897 Claflin, Alan A.....Littleton, Mass.  
1891 Clapp, George H.....375 Water St., Pittsburg, Pa.  
1896 Clark, Arthur W.....Const ocken, Pa.  
1897 Clark, Edmund .....105 Beech St., Flushing, N. Y.  
1898 Clark, Harry W.....Room 502, State House, Boston, Mass.  
1891 Clarke, F. W .....Geol. Survey, Washington, D. C.  
1895 Clarke, Thomas.....Bureau of Animal Industry, Biochemic  
Div., Washington, D. C.  
1898 Clement, Arthur A.....Amer. Cotton Oil Co., 277 Dearborn St.,  
Chicago, Ill.  
1899 Clements, Frank O .....Pa. R. R. Chem. Lab., Altoona, Pa.  
1894 Cleveland, W. P.....Joplin, Mo.  
1899 Closson, C. D .....Green Cons. Copper Co., Box 578, Bisbee,  
Ariz.  
1900 Cluff, Clarence B.....6608 Stewart Ave., Chicago, Ill.  
1893 Coates, Charles E., Jr :.....Louisiana State Univ., Baton Rouge, La.  
1895 Cobleigh, W. M.....Montana State College, Bozeman, Mont.  
1897 Coblentz, Virgil.....115 W. 68th St., N. Y. City.  
1898 Coburn, Arthur S .....49 Oak St., Lowell, Mass.  
1898 Coburn, D. L.....177 State St., Boston, Mass.  
1894 Cochran, C. B .....514 S. High St., West Chester, Pa.



- 1898 Cochrane, A. Lynde ..... Care of Cochrane Chem. Co., Everett, Mass.
- 1900 Cockrill, Irvin ..... Bozeman, Mont.
- 1899 Coggeshall, George W. .... 11 Prescott Hall, Cambridge, Mass.
- 1899 Coit, J. Milner ..... St. Paul's School, Concord, N. H.
- 1881 Colby, Albert Ladd ..... Bethlehem Steel Co., South Bethlehem, Pa.
- 1897 Colby, Edward A ..... Care of Baker Platinum Wks., Newark, N. J.
- 1900 Colley, Bernard T. .... Care of C. K. C. S. and R. Co., Argentine, Kas.
- 1898 Collins, John A., Jr ..... Atlantic Mills, Lawrence, Mass.
- 1898 Comey, Arthur M. .... 54 Concord Ave., Cambridge, Mass.
- 1897 Commiskey, Archibald F .... 155 6th Ave., Brooklyn, N. Y.
- 1891 Congdon, E. A. .... Drexel Institute, Philadelphia, Pa.
- 1899 Conner, Samuel D ..... Expt. Station, Lafayette, Ind.
- 1894 Conradson, P. H. .... Galena Oil Works, Franklin, Pa.
- 1899 Converse, Wm. A ..... 29-33 Rialto Bldg., Chicago, Ill.
- 1898 Cook, A. D. .... N. Y. State Agr. Expt. Sta., Geneva, N. Y.
- 1899 Cook, Charles G. .... Boys' High School, Brooklyn, N. Y.
- 1899 Cook, Robert A. .... New Brunswick, N. J.
- 1893 Cornelison, R. W. .... Care of McKenzie Bros. & Hill, Bloomfield, N. J.
- 1899 Corse, Wm. Malcolm ..... 3553 Bogart Ave., Avondale, Cincinnati, O.
- 1898 Cottle, George T ..... 39 Curtis Ave., Wallingford, Conn.
- 1892 Couch, Guy E ..... Hartwell, Hamilton Co., O.
- 1894 Coutie, William ..... 2129 7th Ave., Troy, N. Y.
- 1898 Cowen, George A ..... 26 Adelaide St., Jamaica Plain, Boston, Mass.
- 1898 Crafts, James M ..... Mass. Inst. Tech., Boston, Mass.
- 1900 Craig, Archibald G ..... 6112 Station St., Pittsburg, Pa.
- 1893 Crampton, C. A. .... Treas. Dept., Washington, D. C.
- 1899 Crane, Frederick ..... 28 Hillside Ave., Montclair, N. J.
- 1896 Crane, Wm. H. .... 20 W. 9th St., Cincinnati, O.
- 1900 Cratty, John M ..... Chem. Lab., Navy Yard, Norfolk, Va.
- 1897 Craver, Harrison W. .... Care of Schoenberger Steel Co., Pittsburg, Pa.
- 1894 Crobaugh, Frank L ..... 17 Bratenahl Building, Cleveland, O.
- 1898 Crocker, Charles S. .... 23 Beach St., Pawtucket, R. I.
- 1900 Croftan, Alfred C ..... Vandevort Block, Pasadena, Cal.
- 1891 Crumbie, Wm. D ..... U. S. Lab., 641 Washington St., N. Y. City.
- 1900 Cuadrado, Gaston A. .... Calle de la Habana 112, Habana, Cuba.

- 1898 Culmann, Julius ..... 400 W. 153rd St., N. Y. City.
- 1899 Curtis, Marvin ..... 123 California St., San Francisco, Cal.
- 1896 Cushman, Allerton S. .... Bryn Mawr College, Bryn Mawr, Pa.
- 1894 Cutter, W. P. .... Library U. S. Dep't Agr., Washington,  
D. C.
- 1896 Cutts, Henry E ..... 65 Columbia Heights, Brooklyn, N. Y.
- 1897 **DAGGETT**, W. W. .... Care of Bertha Mineral Co., Box 35, Pu-  
laski, Va.
- 1900 Dailey, J. Glanding ..... Care of Ledoux & Co., 99 John St., N. Y.  
City.
- 1893 Dains, F. B. .... 2421 Dearborn St., Chicago, Ill.
- 1897 Dales, Benton ..... Box 1203, Cascadilla Place, Ithaca, N. Y.
- 1893 Daniells, Wm. W. .... Univ. of Wis., Madison, Wis.
- 1886 Davenport, B. F. .... 161 Tremont St., Boston, Mass.
- 1895 Davidson, George M. .... Chi. & N. W. Ry., Testing Dept., Chi-  
cago, Ill.
- 1900 Davis, Charles B. .... Care of Dr. Wyatt, 39 S. William St.  
N. Y. City.
- 1896 Davis, Floyd ..... 316-317 Iowa Loan and Trust Bldg., Des  
Moines, Iowa.
- 1900 Davis, Robert S. .... 1330 12th Ave., Altoona, Pa.
- 1893 Davis, Wm. Walley, Jr. .... Care of Va. I. C. and C. Co., Bristol, Va.  
Tenn.
- 1894 Davison, John M. .... 340 Oxford St., Rochester, N. Y.
- 1897 Davoll, David L. .... Care Peninsular Sugar Refining Co.  
Caro, Mich.
- 1898 Day, David T. .... U. S. Geol. Survey, Washington, D. C.
- 1894 Dean, Wm. H. .... 89 W. River St., Wilkesbarre, Pa.
- 1894 De Benneville, James S. .... University Club, 1510 Walnut St., Phila-  
delphia, Pa.
- 1898 Deck, James J. .... Georgetown Univ., Georgetown, D. C.
- 1894 DeConinck, Frank ..... 102 Ellis St., San Francisco, Cal.
- 1895 DeFremery, James L. .... 44 Broadway, N. Y. City.
- 1890 Deghuée, Joseph A. .... 247 Harrison St., Brooklyn, N. Y.
- 1900 Denham, Henry H. .... 146 N. Pearl St., Buffalo, N. Y.
- 1891 Dennis, L. M. .... Cornell University, Ithaca, N. Y.
- 1897 Derby, W. G. .... Care of Nichols Chem. Co., Laurel Hill,  
N. Y.
- 1895 DeRoode, Rudolf ... Care of International Paper Co., Glens  
Falls, N. Y.
- 1893 De Schweinitz, E. A. .... Biochemic Lab., Dept. of Agr., Washing-  
ton, D. C.
- 1895 Desper, E. W. .... 39 Westminster St., Worcester, Mass.
- 1893 Dewey, F. P. .... 702 9th St., N. W., Washington, D. C.
- 1898 Dickerman, Judson C. .... 10 Minot St., Woburn, Mass.

- 1893 Dickerson, Edward N ..... 141 Broadway, N. Y. City.
- 1899 Dickson, J. C. .... 218 N. Jefferson St., Muncie, Ind.
- 1898 Dickson, W. E. .... Care of Spearman Iron Co., Sharpsville, Pa.
- 1899 Dieckmann, Otto ..... 1182 Harrison Ave., Cincinnati, O.
- 1900 Diehl, O. C. .... Biological Lab., Parke, Davis & Co., Detroit, Mich.
- 1899 Divine, Robert E. .... Hamburg, Erie Co., N. Y.
- 1899 Dixon, John B. .... Collins House, Glens Falls, N. Y.
- 1897 Doan, Martha ..... M. T. High School, Indianapolis, Ind.
- 1895 Dobbin, Leonard ..... Univ. of Edinburgh, Edinburgh, Scotland.
- 1891 Dodge, F. E. .... Lansdowne, Pa.
- 1895 Doerflinger, Wm. F. .... 85 Lafayette Ave., Brooklyn, N. Y.
- 1898 Doggett, Chas. S. .... Niagara Falls, N. Y.
- 1891 Dohme, Alfred R. L. .... Care of Sharp & Dohme, Mfg. Chem., Baltimore, Md.
- 1894 Doolittle, O. S. .... 130 N. 5th St., Reading, Pa.
- 1900 Doolittle, R. E. .... State Dairy and Food Com., Lansing, Mich.
- 1876 Doremus, Chas. A. .... 17 Lexington Ave., N. Y. City.
- 1894 Dorr, John V. N. .... Golden Gate M. and M. Co., Deadwood, S. D.
- 1895 Dorset, F. Marion ..... Biochemic Lab., Dept. of Agr., Washington, D. C.
- 1879 Doscher, Henry ..... 122 E. 37th St., N. Y. City.
- 1900 Douglas, William ..... Plantation Diamond, Demerara, British Guiana.
- 1895 Dow, Allan W. .... District Building, Washington, D. C.
- 1898 Dow, Herbert H. .... Midland, Mich.
- 1900 Downey, James E. .... High School, Holyoke, Mass.
- 1898 Doyle, Aida M. .... 1902 Third St., N. W., Washington, D. C.
- 1898 Drake, C. F. .... 4555 Lake Ave., Chicago, Ill.
- 1894 Drew, Charles W. .... 505 Century Building, Minneapolis, Minn.
- 1892 Drown, T. M. .... Lehigh Univ., South Bethlehem, Pa.
- 1886 Drummond, I. W. .... 436 W. 22nd St., N. Y. City.
- 1898 Duckworth, Harry S. .... Cocheco Mfg. Co., Dover, N. H.
- 1876 **DUDLEY, CHARLES B.** .... Drawer 334, Altoona, Pa.
- 1890 Dudley, Wm. L. .... Vanderbilt University, Nashville, Tenn.
- 1897 Duffield, Samuel P. .... Dearborn, Wayne Co., Mich.
- 1881 Dunham, E. K. .... 338 E. 26th St., N. Y. City.
- 1898 Dunlap, Fred. L. .... Worcester Poly. Inst., Worcester, Mass.
- 1900 Dunn, Willis A. .... Santa Ana, Cal.
- 1894 Dunnington, F. P. .... Univ. of Va., Charlottesville, Va.
- 1895 Du Pont, Francis G. .... Wilmington, Del.
- 1893 Du Pont, Pierre S. .... The Johnson Co., Lorain, O.

- 1898 Durfee, Winthrop C.....81 Sedgwick St., Jamaica Plain, Boston, Mass.
- 1898 Durkee, Wm. C.....392 Boylston St., Boston, Mass.
- 1899 Duryea, Chester B .....Sioux City, Iowa.
- 1900 Dustin, Guy K.....30 Lenango St., Binghamton, N. Y.
- 1899 Du Vivier, Ernest H .....22 Warren St., N. Y. City.
- 1897 EACHUS, Charles .....Coatesville, Pa.
- 1900 Earle, Richard B.....403 Craigie Hall, Cambridge, Mass.
- 1894 Eavenson, Alban .....2013 Vine St., Philadelphia, Pa.
- 1900 Ebaugh, W. Clarence.....3741 Lancaster Ave., Philadelphia, Pa.
- 1894 Eberman, William S .....Encampment, Wyoming.
- 1894 Eccles, Robert G.....191 Dean St., Brooklyn, N. Y.
- 1899 Eckfeldt, Jacob B .....U. S. Mint, Philadelphia.
- 1894 Eddy, Harrison P.....City Hall, Worcester, Mass.
- 1897 Edgar, C. G .....565 Woodward Ave., Detroit, Mich.
- 1899 Edgerly, D. W.....Care Chilton Paint Co., College Point, N. Y.
- 1893 Edson, Hubert.....Patterson, La.
- 1895 Ehrenfeld, Charles H.....Collegiate Institute, York, Pa.
- 1894 Eichberg, Julius H.....Groton Bldg., 7th and Race Sts., Cincinnati, O.
- 1879 Eimer, August.....Third Ave. and 18th St., N. Y. City.
- 1898 Ekeley, John B .....St. Paul's School, Garden City, N. Y.
- 1899 Ellery, James B.....322 Pine St., Steelton, Pa.
- 1898 Elliott, A. H.....4 Irving Pl., N. Y. City.
- 1896 Elliott, Edward C.....212 W. 9th St., Leadville, Colo.
- 1893 Elliott, Russell .....34 S. Main St., Dayton, O.
- 1891 Ellis, G. H .....163 Randolph St., Chicago, Ill.
- 1898 Ellms, Joseph W.....Lab. Com. of Water Wks., E. Court and Martin Sts., Cincinnati, O.
- 1898 Elworthy, H. S .....2 Peel Terrace, Havre-des-Pas, Jersey, Channel Islands.
- 1898 Ely, Charles R.....Gallaudet College, Washington, D. C.
- 1894 Ely, G. S.....Patent Office, Washington, D. C.
- 1895 Emerson, Wm. H.....Georgia School of Technology, Atlanta, Ga.
- 1900 Emery, A. L.....Palo Alto, Cal.
- 1890 Emmens, Stephen H .....1 Broadway, N. Y. City.
- 1876 Endemann, Hermann .....23 William St., N. Y. City.
- 1892 Enequist, John.....556 Greene Ave., Brooklyn, N. Y.
- 1898 Engle, W. D.....University Park, Col.
- 1895 Enright, Bernard.....330 E. 4th St., So. Bethlehem, Pa.
- 1894 Escher, Paul.....Care of Acker Process Co., Niagara Falls, N. Y.
- 1899 Eustis, Allen C .....1410 Jackson Ave., New Orleans, La.
- 1897 Evans, Ernest .....Woodward Iron Co., Woodward, Ala.

- 1895 Fosdick, E. H ..... 1505 S. Grand Ave., Los Angeles, Cal.  
1897 Fossler, Mary L ..... 734 N. 9th St., Lincoln, Neb.

- 1894 Fourneaux, Emile A.....Box 284, Pawtucket, R. I.  
 1896 Fox, H. W .....Care of De Lar Mar's Mercur Mines Co.,  
 Mercur, Utah.  
 1897 Francis, John M .....Care of Parke, Davis & Co., Detroit,  
 Mich.  
 1891 Frank, J. W .....734 E. 14th St., N. Y. City.  
 1893 Frankforter, George B .....Dept. of Chem., Univ. of Minn., Minne-  
 apolis, Minn.  
 1899 Franklin, Arthur I.....100 Canal St., Cleveland, Ohio.  
 1895 Franklin, Edward C .....Lawrence, Kan.  
 1900 Frazee, F. H.....416 Concord Ave., Detroit, Mich.  
 1891 Frear, William.....State College, Pa.  
 1897 Freer, Paul C.....Univ. of Mich., Ann Arbor, Mich.  
 1893 Frerichs, F. W.....Herf & Frerichs Chem. Co., St. Louis,  
 Mo.  
 1888 Fries, H. H.....92 Reade St., N. Y. City.  
 1893 Fries, J. August.....State College, Pa.  
 1894 Froehling, Henry .....17 S. 12th St., Richmond, Va.  
 1895 Frohman, Edward D .....Care of O. Hommel & Co., 23d St and  
 Penn Ave., Pittsburg, Pa.  
 1892 Frost, Howard V.....Arlington, Mass.  
 1894 Fuelling, John L.....New Durham, N. J.  
 1896 Fullam, Frank L.....U. S. Naval Torpedo Station, Newport,  
 R. I.  
 1894 Fuller, Frederick D .....14 Elmwood Ave., Geneva, N. Y.  
 1895 Fuller, George W.....220 Broadway, N. Y. City.  
 1894 Fulmer, Elton .....Agr. Expt. Sta., Pullman, Wash.  
 1898 GABRIEL, George A.....Box 390, Cumberland Mills, Me.  
 1898 Gage, Stephen DeM.....Expt. Sta., Lawrence, Mass.  
 1894 Gaines, Richard H.....Dept. of Agr., Richmond, Va.  
 1893 Gallaher, Phil. C.....120 W. 6th St., Leadville, Colo.  
 1899 Gallivan, Frank B.....Polytechnic Institute, Brooklyn, N. Y.  
 1897 Gallup, Harriet T .....Kodak Park, Rochester, N. Y.  
 1900 Garduño, Jesus .....Aguascalientes, Mexico.  
 1899 Garrigues, W. E .....1123 Broadway, N. Y. City.  
 1894 Gascoyne, W. J.....36 S. Holliday St., Baltimore, Md.  
 1895 Gaylord, W. K .....Throop Polytechnic Institute, Pasadena,  
 Cal.  
 1886 Geisler, J. F.....Room 38, 6 Harrison St., N. Y. City.  
 1893 Genth, F. A., Jr .....103 N. Front St., Philadelphia, Pa.  
 1898 Georgii, Max .....606 F St., N. W., Washington, D. C.  
 1898 Gere, Mariel C.....849 D St., Lincoln, Neb.  
 1900 Gerlach, Oscar.....Mich. Port. Cem. Co., Coldwater, Mich.  
 1897 Getman, F. H .....196 Atlantic St., Stamford, Conn.  
 1900 Getz, Wm. H .....Office of City Chemist, 1141 Market St.,  
 St. Louis, Mo.

- 1892 Griffith, S. H ..... U. S. Naval Museum of Hygiene, Wash-  
ington, D. C.

- 1895 Grindley, H. S.....918 W. Green St., Urbana, Ill.  
 1898 Gronemeyer, Herman H.....731 Giddings Ave., Cleveland, O.  
 1899 Gross, Abraham .....341 Oakland Ave., Pittsburg, Pa.  
 1894 Grosvenor, W. M., Jr .....Box 183, Englewood, N. J.  
 1899 Gruenberg, Benjamin C .....U. S. Lab., 641 Washington St., N. Y.  
 City.  
 1899 Gruener, Hippolyte .....Adelbert College, Cleveland, O.  
 1890 Gudeman, Edward.....Care of Glucose Sugar Ref. Co., Taylor  
 St. and the River, Chicago, Ill.  
 1898 Guess, Harry A.....Care of Ottawa Gold Milling and Mining  
 Co., Ltd., Keewatin, Ontario.  
 1895 Guild, Frank N.....Univ. of Arizona, Tucson, Ariz.  
 1897 Gustin, G. H .....216 Murray St., Elizabeth, N. J.  
 1876 **HABIRSHAW, W. M** ....Care of Glenwood Works, Yonkers, N. Y.  
 1891 Haigh, D. L .....11 Broadway, N. Y. City.  
 1899 Haigh, Frederic.....677 E. 24th St., Paterson, N. J.  
 1894 Haines, Reuben.....Haines and Chew Sts., Germantown,  
 Philadelphia, Pa.  
 1892 Haines, Walter S .....Rush Med. College, Chicago, Ill.  
 1880 Hale, Albert C.....551 Putnam Ave., Brooklyn, N. Y.  
 1898 Hale, Frank M .....137 Glenwood Ave., Jersey City, N. J.  
 1895 Hall, C. A.....3220 Powelton Ave., Philadelphia, Pa.  
 1896 Hall, Clarence.....Care of Aetna Powder Co., Aetna, Ind.  
 1900 Hall, Everett J.....Passaic, N. J.  
 1892 Hall, J. G .....Natrona, Pa.  
 1894 Hall, L. B .....Haverford College, Haverford, Pa.  
 1888 Hall, R. W. ....Havemeyer Lab., University Heights,  
 N. Y. City.  
 1898 Hall, Wm. T .....Mass. Inst. Tech., Boston, Mass.  
 1881 Hallock, A. P.....440 First Ave., New York City.  
 1900 Hamilton, Louis P .....222 E. Beaux St., Washington, Pa.  
 1900 Hamlin, Addison .....25 5th St., Bangor, Me.  
 1894 Hancock, David .....Box 12, Birmingham, Ala.  
 1900 Hancock, W. J.....Erasmus Hall High School, Brooklyn,  
 N. Y.  
 1899 Hand, W. F .....Agricultural College, Miss.  
 1893 Handy, James O.....325 Water St., Pittsburg, Pa.  
 1896 Hanks, Abbot A .....531 California St., San Francisco, Cal.  
 1898 Hanna, D. C.....4262 Parkside Ave., Philadelphia, Pa.  
 1896 Hanna, George B .....Box 26, Charlotte, N. C.  
 1899 Hanson, Charles A.....Care of Fleischmann and Co., Riverside,  
 Cincinnati, O.  
 1898 Hapgood, Charles W.....Abattoir, Brighton, Mass.  
 1899 Hardenburgh, Louis M.....Iron Mountain, Mich.  
 1876 Hardin, M. B.....Clemson College, S. C.



- 1897 Hardin, W. L. .... John Harrison Lab., Univ. of Pa., Philadelphia, Pa.
- 1897 Harding, E. P. .... 22 Landhaus Strasse, Heidelberg, Germany.
- 1894 Hare, C. L. .... Box 145, Auburn, Ala.
- 1898 Hargrove, Julian O. .... 3310 N St., N. W., Washington, D. C.
- 1897 Harms, Armin ..... Care of Compania Metallurgica Mexicana, San Luis Potosi, Mexico.
- 1897 Harold, Joseph F. X ..... 636 Spruce St., Philadelphia, Pa.
- 1897 Harper, C. A. .... 2139 Gilbert Ave., Cincinnati, O.
- 1898 Harper, H. W. .... Univ. of Texas, Austin, Texas.
- 1894 Harrington, B. J. .... 295 University St., Montreal, Canada.
- 1897 Harrington, E. M. .... Aetna, Lake Co., Ind.
- 1898 Harris, C. D. .... Agr. Expt. Sta., Raleigh, N. C.
- 1890 Harris, E. P. .... The Lakewood School, Lakewood, N. J.
- 1899 Harris, Isham G. .... H. R. State Hospital, Poughkeepsie, N. Y.
- 1895 Harris, J. R. .... Care of Tenn. C. I. & R. Co., 1918-1920 Morris Ave., Birmingham, Ala.
- 1895 Harrison, J. B. .... Gov. Lab., Georgetown, Demerara, British Guiana.
- 1900 Harrold, E. E. .... Ohio State Univ., Columbus, O.
- 1896 Harsh, S. A. .... Gould, Lewis and Clarke Co., Mont.
- 1890 Hart, Edward ..... Lafayette College, Easton, Pa.
- 1898 Hart, Edwin B. .... Agr. Expt. Station, Geneva, N. Y.
- 1900 Hartford, James ..... 100 William St., N. Y. City.
- 1900 Hartman, Wm. E. .... Kalamazoo Gas Works, Spring and Pitcher Sts., Kalamazoo, Mich.
- 1896 Hartwell, Burt L. .... Kingston, R. I.
- 1899 Hartzell, Harry S. .... 22 N. 8th St., Allentown, Pa.
- 1899 Haskins, Henri D. .... Expt. Station, Amherst, Mass.
- 1900 Hatchett, Roger H. .... Care C. K. C. S. and R. Co., Argentine, Kas.
- 1892 Havemeyer, H. O. .... 117 Wall St., N. Y. City.
- 1900 Havens, Franke S. .... 9-13 Mercer St., N. Y. City.
- 1898 Hawkins, H. .... Oakland, Bergen Co., N. J.
- 1895 Hayes-Campbell, J. .... 514 E. 6th St., Newport, Ky.
- 1897 Haynes, D. O. .... Box 1483, N. Y. City.
- 1893 Hays, Joseph A. .... 147 S. 18th St., Pittsburg, Pa.
- 1897 Haywood, John K. .... Dept. of Agr., Div. of Chem., Washington, D. C.
- 1899 Haywood, W. G. .... Expt. Station, Raleigh, N. C.
- 1899 Hazard, F. R. .... Solvay Process Co., Syracuse, N. Y.
- 1894 Hazen, Allen ..... 220 Broadway, N. Y. City.
- 1894 Heath, George L. .... Cal. & Hecla Smelting Works, S. Lake Linden, Mich.

- 1893 Hebden, John C ..... 40 S. Water St., Providence, R. I.  
1893 Heerlein, Robert ..... Natrona, Pa.  
1900 Heidenhain, H. .... Royal Baking Powder Co., Kent Ave and  
Morton St., Brooklyn, N. Y.  
1897 Heileman, W. H ..... Pullman, Wash.  
1898 Henderson, Wm. E. .... Ohio State Univ., Columbus, O.  
1900 Herger, Chas. G ..... 11 Putnam St., Buffalo, N. Y.  
1897 Hero, Ann ..... Pratt Institute, Brooklyn, N. Y.  
1876 Herreshoff, J. B. F. .... 19 Pierrepont St., Brooklyn, N. Y.  
1898 Herrick, Rufus F ..... Box 1768, Boston, Mass.  
1894 Herrick, Wm. Hale ..... 22-24 Morris St., Jersey City, N. J.  
1894 Hershey, Aldus N. .... Care of Sharp & Dohme, Baltimore, Md.  
1894 Herty, Charles H. .... Athens, Ga.  
1900 Hess, Henry W ..... Chemist, Toledo Gas Light and Coke Co.  
(Works), Toledo, O.  
1899 Hess, Wm. H. .... State Food Dept., Lansing, Mich.  
1899 Hesse, Bernhard C. .... 128 Duane St., N. Y. City.  
1893 Hewitt, Edward R ..... Garden City, N. Y.  
1897 Hewson, James H. .... 872 Broad St., Newark, N. J.  
1894 Hibbard, P. L ..... 525 Clayton St., Waukegan, Ill.  
1896 Hicks, Edwin F ..... 203 W. 81st St., N. Y. City.  
1897 Higbee, H. H. .... Hamilton College, Clinton, N. Y.  
1900 Hill, Edwin A ..... Classification Division, U. S. Patent Office,  
Washington, D. C.  
1899 Hill, Henry B ..... Harvard Univ., Cambridge, Mass.  
1898 Hill, Herbert H. .... Box 222, Andover, Mass.  
1891 Hill, Herbert M ..... Univ. of Buffalo, 24 High St., Buffalo,  
N. Y.  
1898 Hill, Wm. G., Jr. .... 84 Converse Ave., Malden, Mass.  
1893 Hillebrand, W. F ..... Geol. Survey, Washington, D. C.  
1893 Hills, Wm. B ..... 688 Boylston St., Boston, Mass.  
1900 Hillyer, Homer W ..... 1811 Adams Ave., Madison, Wis.  
1897 Hillyer, Wm. E. .... Asst. Chem., B. & O. R. R., Mt. Clare,  
Baltimore, Md.  
1899 Hiltner, M. E ..... 1301 N St., Lincoln, Neb.  
1895 Hiltner, R. S. .... Univ. of Neb., Lincoln, Neb.  
1899 Hinckley, J. Fred ..... Care of B. T. Babbitt and Co., N. Y. City.  
1877 Hindley, R. C ..... 1328 Carlisle Ave., Racine, Wis.  
1895 Hinds, J. I. D ..... Lebanon, Tenn.  
1894 Hitchcock, Fanny R. M. .... 4038 Walnut St., Philadelphia, Pa.  
1895 Hobbs, Perry L. .... Western Reserve Med. College, Cleveland,  
O.  
1893 Hochstetter, Robert W ..... Oak St. and Bellevue Ave., Mt. Auburn,  
Cincinnati, O.  
1893 Hodges, G. C. .... High School, Utica, N. Y.

- 1893 Hodges, H. B. .... Office of Purchasing Agt., L. I. R. R.,  
Long Island City, N. Y.
- 1899 Hodgson, Eugene H ..... 848 President St., Brooklyn, N. Y.
- 1898 Hoff, Karl ..... 608 E. 4th St., Anaconda, Mont.
- 1894 Hoffmann, Philip C ..... Fairfield Station 217, Baltimore, Md.
- 1900 Hofmann, Ottokar ..... Argentine, Kas.
- 1899 Holden, E. F ..... 32 Lake Ave., Melrose, Mass.
- 1894 Hollinshead, W. H ..... Vanderbilt Univ., Nashville, Tenn.
- 1898 Hollis, Frederick S ..... 90 Erie Ave., Newton Highlands, Mass.
- 1898 Holman, George M ..... 52 Pleasant St., Fitchburg, Mass.
- 1894 Holter, George L ..... Stillwater, Oklahoma.
- 1893 Holton, Fred. A ..... Brookland, D. C.
- 1895 Homburg, Fred ..... 104 W. Clifton Ave., Cincinnati, O.
- 1876 Homer, C. S., Jr ..... 57 Broadway, N. Y. City.
- 1900 Hooker, Samuel C ..... Spreckels Sugar Ref., Philadelphia, Pa.
- 1900 Hopkins, Arthur J ..... Amherst College, Amherst, Mass.
- 1896 Hopkins, Cyril G ..... 907 S. Wright St., Champaign, Ill.
- 1897 Hopkins, Erastus ..... 177 State St., Boston, Mass.
- 1895 Hopkins, N. Monroe ..... 1833 Jefferson Pl., Washington, D. C.
- 1894 Horne, Wm. D ..... Yonkers, N. Y.
- 1898 Horsford, Roger F ..... Care Amer. Bell Telephone Co., 125 Milk  
St., Boston, Mass.
- 1899 Horton, E. G ..... State Board of Health, Columbus, O.
- 1893 Hoskins, Wm ..... Room 55, 81 S. Clark St., Chicago, Ill.
- 1899 Hough, George J ..... Cerralvo, Nuevo Leon, Mexico.
- 1895 Howard, Charles D ..... Morgantown, W. Va.
- 1887 Howard, Curtis C ..... 97 Jefferson Ave., Columbus, O.
- 1898 Howard, Henry ..... 175 Mountfort St., Brookline, Mass.
- 1897 Howe, Elmer P ..... Exchange Building, 53 State St., Boston,  
Mass.
- 1893 Howe, Jas. Lewis ..... Washington & Lee Univ., Lexington, Va.
- 1899 Howell, E. V ..... Chapel Hill, N. C.
- 1898 Hughes, Raymond M ..... Miami Univ., Oxford, O.
- 1900 Hulett, George A ..... 706 S. Thayer St., Ann Arbor, Mich.
- 1900 Hummel, John A ..... State Capitol, St. Paul, Minn.
- 1899 Humphrey, Richard L ..... 413 Girard Building, Philadelphia, Pa.
- 1895 Hunicke, H. A ..... 3532 Victor St., St. Louis, Mo.
- 1897 Hunter, J. Rufus ..... Richmond College, Richmond, Va.
- 1897 Huntington, Harwood ..... Wool Exchange, 260 W. Broadway, N. Y.  
City.
- 1896 Hunziker, Aug ..... Care of Weidman Silk Dyeing Co., Pat-  
erson, N. J.
- 1897 Hurlburt, E. B ..... Care of The J. B. Williams Co., Glaston-  
bury, Conn.
- 1893 Hurley, John ..... Little Falls, N. Y.

- 1893 Hurty, J. N.....202 N. Pennsylvania St., Indianapolis, Ind.
- 1893 Huston, H. A.....Lafayette, Ind.
- 1894 Hyde, F. S .....215 Schermerhorn St., Brooklyn, N. Y.
- 1897 Hyde, Henry St. J .....210 E. 18th St., N. Y. City.
- 1895 IRISH, Cyrus W .....91 Fort Hill Ave., Lowell, Mass.
- 1900 Irwin, Edward P.....1612 Madison Ave., Kansas City, Mo.
- 1898 Isaacs, A. S .....1214 Sheffield St., Allegheny, Pa.
- 1898 JACKSON, C. L .....Harvard Univ., Cambridge, Mass.
- 1898 Jackson, Daniel D .....96 Prospect Place, Brooklyn, N. Y.
- 1900 Jackson, Florence .....Wellesley College, Wellesley, Mass.
- 1898 Jacobs, Charles B .....Ampère, N. J.
- 1898 James, George A.....Selby P. O., Contra Costa Co., Cal.
- 1893 James, George W .....Care of Richards & Co., Chicago, Ill.
- 1898 James, Joseph H.....Sault Ste. Marie, Ontario.
- 1894 James, Lawrence S.....32 Hawley St., Boston, Mass.
- 1895 Jameson, A. H.....Care of Logan Mfg. Co., Phoenixville, Pa.
- 1900 Jandrier, Edmond.....Peace Dale, R. I.
- 1891 Jarman, J. L.....Emory, Va.
- 1894 Jayne, H. W.....931 N. Broad St., Philadelphia, Pa.
- 1898 Jenkins, Charles D.....32 Hawley St., Boston, Mass.
- 1899 Jenkins, Ellery D.....Lowell Fertilizer Co., Lowell, Mass.
- 1897 Jenks, Stillman G .....Kalamazoo College, Kalamazoo, Mich.
- 1898 Jennings, Walter L .....Poly. Inst., Worcester, Mass.
- 1900 Jessup, Alfred E .....Office of Supervising Architect, Treas. Dept., Washington, D. C.
- 1898 Jessurun, David .....Alma Sugar Co., Alma, Mich.
- 1894 Jewett, Frank F .....Oberlin College, Oberlin, O.
- 1894 Job, Robert.....Care of Philadelphia & Reading R. R. Co., Reading, Pa.
- 1894 Johns, John .....306 Toone St., Baltimore, Md.
- 1895 Johnson, Edward S .....315 Highland Ave., Syracuse, N. Y.
- 1895 Johnson, Emil F.....96-98 Maiden Lane, N. Y. City.
- 1900 Johnson, Flournoy C .....714 Union St., New Orleans, La.
- 1898 Johnson, George A.....220 Broadway, N. Y. City.
- 1895 Johnson, Jesse F.....Care of Hamilton Powder Co., Montreal, Canada.
- 1892 Johnson, Otis C.....730 Thayer St., Ann Arbor, Mich.
- 1876 Johnson, S. W.....Drawer 101, New Haven, Conn.
- 1900 Johnson, Treat B .....Care of Phillips, Westville, Conn.
- 1897 Jones, A. B .....Lock Box 741, Pittsburg, Pa.
- 1897 Jones, Arthur O .....2315 Highland Ave., Walnut Hills, Cincinnati, O.
- 1893 Jones, Clemens C .....908 W. Franklin St., Richmond, Va.
- 1899 Jones, Fred. W .....Barwick, near Ware, Herts, England.

- 1892 Jones, Jesse.....Care of Wm. Cramp & Sons, Philadelphia, Pa.
- 1895 Jones, L. J. W ..... Amer. Sm. and Ref. Co., Omaha, Neb.
- 1890 Jones, R. W ..... University, Lafayette Co., Miss.
- 1896 Jones, W. J., Jr.....Asst. State Chemist, Lafayette, Ind.
- 1898 Jones, Wm. App ..... 145 W. 82d St., N. Y. City.
- 1897 Joslin, Carrie E.....930 Curtis St., Walnut Hills, Cincinnati, O.
- 1898 Joüet, C. H.....Roselle, Union Co., N. J.
- 1893 Julian, Frank ..... Great Northern Shops, St. Paul, Minn.
- 1898 KAHLENBERG, Louis.... 306 Lake St., Madison, Wis.
- 1898 Kastle, Joseph H ..... State College of Kentucky, Lexington, Ky.
- 1899 Kaufmann, Wm. P.....Gov. Lab., Georgetown, Demerara, British Guiana.
- 1891 Keator, Charles E.....Cor. Nostrand and Park Aves., Brooklyn, N. Y.
- 1894 Kebler, Lyman F ..... 35 Poplar St., Philadelphia, Pa.
- 1894 Kedzie, Frank S ..... 414 Ottawa St., Lansing, Mich.
- 1894 Kedzie, R. C ..... Agr. College, Ingham Co., Mich.
- 1895 Keiser, E. H..... Washington Univ., St. Louis, Mo.
- 1895 Keller, Charles ..... 113 Biddle Ave., Station D, Pittsburg, Pa.
- 1899 Keller, Cornelius ..... Apartado A, Aguascalientes, Mexico.
- 1894 Keller, Edward.....Box 1724, Baltimore, Md.
- 1894 Keller, Harry F ..... 512 N. 34th St., Philadelphia, Pa.
- 1894 Kelley, J. H..... 315 N. Vine St., Nashville, Tenn.
- 1899 Kelly, Daniel J ..... Room 39, Patent Office, Washington, D. C.
- 1899 Kelly, F. G ..... Care of Tenn. C. I. and R. Co., Birmingham, Ala.
- 1894 Kenan, W. R., Jr ..... Care of Traders' Paper Co., Lockport, N. Y.
- 1888 Kendall, E. Dwight..... 1109 Park Pl., Brooklyn, N. Y.
- 1899 Kendall, Robert E..... 96 Warren St., Glens Falls, N. Y.
- 1894 Kenney, C. Belle..... Quincy Mansion School, Wollaston, Mass.
- 1885 Kent, Walter H..... 300 Washington St., Brooklyn, N. Y.
- 1898 Kessler, J. J., Jr ..... Testing Lab., General Electric Co., Schenectady, N. Y.
- 1894 Kilgore, B. W ..... Raleigh, N. C.
- 1887 King, F. T..... 91 Columbia Heights, Brooklyn, N. Y.
- 1892 Kingsford, Thomas P ..... Oswego Starch Factory, Oswego, N. Y.
- 1891 Kinnicutt, L. P ..... 77 Elm St., Worcester, Mass.
- 1894 Kirchgasser, W. C ..... 74 and 76 Laight St., N. Y. City.
- 1891 Kirchmaier, G. A ..... Adams and Huron Sts., Toledo, O.
- 1893 Kirk, David M ..... 910 Duquesne Way, Pittsburg, Pa.

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- 1898 LeCléar, Thom as.....262 5th Ave., N. Y. City.  
 1898 LeClerc, J. Arthur .....Agr. Expt. Station, Geneva, N. Y.  
 1896 Lederle, Ernst J .....471 W. 143d St., N. Y. City.  
 1895 Ledoux, A. R.....98 John St., N. Y. City.  
 1898 Lee, John C . ....Brookline, Mass.  
 1899 Lee, Waldemar .....Passaic, N. J.  
 1878 Leeds, A. R .....Stevens Institute, Hoboken, N. J.  
 1893 Leffmann, Henry .....715 Walnut St., Philadelphia, Pa.  
 1885 Lehmann, G. W .....412 E. Lombard St., Baltimore, Md.  
 1899 Lengfeld, Felix.....Univ. of Chicago, Chicago, Ill.  
 1895 Lenher, Victor .....Univ. of Wis., Madison, Wis.  
 1897 Lenox, L. R.....Stanford Univ., Cal.  
 1896 Lerch, Fred .....Hibbing, Minn.  
 1899 Levene, Phoebus A .....87 Lenox Ave., N. Y. City.  
 1899 Levine, Edmund J .....337 W. 88th St., N. Y. City.  
 1899 Levison, Wallace G.....1435 Pacific St., Brooklyn, N. Y.  
 1900 Lichtenstein, Alfred F.....6 Elmwood Ave., North Adams, Mass.  
 1900 Lihme, C. B .....Care of Ill. Zinc Co., Peru, Ill.  
 1896 Lihme, I. P. ....The Grasselli Chem. Co., Cleveland, O.  
 1892 Lindsay, Wm. B .....Carlisle, Pa.  
 1895 Lindsey, J. B .....Lock Box 217, Amherst, Mass.  
 1895 Linebarger, C. E.....1210 Perry St., Chicago, Ill.  
 1894 Linn, Alvin F .....Wittenberg College, Springfield, O.  
 1899 Linton, J. H.....Care of Tenn. C. I. and R. Co., Birmingham, Ala.  
 1898 Lipman, Jacob G .....Woodbine, N. J.  
 1896 Lippincott, Warren B .....Amer. S. and R. Co., Argentine, Kas.  
 1893 Little, A. D .....7 Exchange Pl., Boston, Mass.  
 1893 Littlewood, J. B .....U. S. Patent Office, Washington, D. C.  
 1898 Livermore, Wm. D.....Washington Mills Co., Lawrence, Mass.  
 1899 Lloyd, George.....52 Dearborn St., Chicago, Ill.  
 1893 Lloyd, J. U.....Court and Plum Sts., Cincinnati, O.  
 1899 Lockwood, Rhodes G.....Care of Davidson Rubber Co., 19 Milk St., Boston, Mass.  
 1889 Loeb, Morris.....118 W. 72nd St., N. Y. City.  
 1900 Loew, Oscar .....Dept. of Agr., Washington, D. C.  
 1900 Logan, Lily.....Howardsville, Va.  
 1893 Long, J. H .....2421 Dearborn St., Chicago, Ill.  
 1899 Longstaff, J. P.....Chem. Dept., Univ. of Edinburgh, Edinburgh, Scotland.  
 1892 Loomis, Horatio .....58 W. 40th St., N. Y. City.  
 1899 Loos, Edward A .....933 N. Front St., Philadelphia.  
 1898 Loos, Hermann A.....119 E. 115th St., N. Y. City.  
 1896 Lord, N. W .....Ohio State Univ., Columbus, O.  
 1898 Lorenz, Henry W. F .....Univ. of Pa., Philadelphia, Pa.

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- 1898 Martin, Merrill A .....U.S. Mint, San Francisco, Cal.  
1893 Martin, O. W .....Hughes High School, Cincinnati, O.  
1896 Martin, Wm. J., Jr .....Davidson, N. C.  
1899 Mason, Francis P .....214 Monadnock Bldg., Chicago, Ill.  
1885 MASON, WM. P .....Rensselaer Poly. Inst., Troy, N. Y.  
1900 Mather, Henry A .....Care of Verde Queen Copper Co., Jerome,  
Ariz.  
1892 Matheson, W. J .....182-184 Front St., N. Y. City.  
1896 Mathews, John A .....4 First Pl., Brooklyn, N. Y.  
1898 Mathewson, E. P .....Establacimiente del Playa Blanca, Antofogasta, Chili, S. A.  
1898 Matthews, J. Merritt .....634 Spruce St., Philadelphia, Pa.  
1894 Maury, George P .....Mount Iron, St. Louis Co., Minn.  
1893 Maxwell, Walter .....Sugar Expt. Sta., Honolulu, Hawaii,  
U. S. A.  
1896 May, George H .....Care of Amer. Pegamoid Co., Hohokus,  
Bergen Co., N. J.  
1896 Maywald, F. J .....72d St. and 10th Ave., Bay Ridge Park,  
Brooklyn, N. Y.  
1895 McBryde, J. Bolton .....Univ. of Tenn., Knoxville, Tenn.  
1894 McCandless, John M .....State Chemist, Atlanta, Ga.  
1899 McCay, Leroy W .....Chem. Lab., Princeton, N. J.  
1900 McClement, Wm. T .....Armour Institute, Chicago, Ill.  
1894 McCurdy, Charles W .....North Yakima, Wash.  
1893 McDonnell, H. B .....Md. Agr. College, College Park, Md.  
1894 McDonnell, M. E .....Box 236, Altoona, Pa.  
1899 McDowell, Alex. H .....457 W. 21st St., N. Y. City.  
1900 McFarland, B. W .....278 Canner St., New Haven, Conn.  
1897 McFarlen, T. J .....New Glasgow, Nova Scotia, Canada.  
1896 McFetridge, Joseph .....Natrona, Pa.  
1897 McGeorge, Arthur .....Care of Chesebrough Mfg. Co., Delevan  
St., Brooklyn, N. Y.  
1890 McGill, J. T .....Vanderbilt Univ., Nashville, Tenn.  
1898 McGilton, Wm. W .....Middlebury College, Middlebury, Vt.  
1893 McGregory, J. F .....Colgate Univ., Hamilton, N. Y.  
1894 McIlhiney, Parker C .....145 E. 23d St., N. Y. City.  
1900 McIntosh, Douglas .....208 E. 61st St., N. Y. City.  
1898 McKelvey, J. Wm .....813 Montgomery St., Jersey City, N. J.  
1883 McKenna, Charles F .....221 Pearl St., N. Y. City.  
1897 McKenzie, R. Monroe .....Box 664, Chicago Heights, Ill.  
1892 McLoughlin, Charles .....874 Broadway, N. Y. City.  
1890 McMurtrie, Wm .....101 W. 81st St., N. Y. City.  
1894 McPherson, Wm., Jr .....Ohio State Univ., Columbus, O.  
1898 McTaggart, James R .....Pittsburg Testing Lab., 325 Water St.,  
Pittsburg, Pa.

- 1896 Meade, Richard K .....Lafayette College, Easton, Pa.  
 1899 Meaker, W. Lathrop .....Longdale, Alleghany Co., Va.  
 1899 Means, R. F.....6 Custom House St., Boston, Mass.  
 1894 Mears, Leverett.....Chem. Lab., Williamstown, Mass.  
 1894 Meeds, Alonzo D.....103 Boston Block, Minneapolis, Minn.  
 1894 Meeker, G. H.....Medico-Chirurgical College, Philadelphia, Pa.  
 1893 Mellen, Edwin D .....1590 Massachusetts Ave., Cambridge, Mass.  
 1892 Menke, A. E.....Fayetteville, Ark.  
 1898 Merigold, Benjamin S.....1691 Cambridge St., Cambridge, Mass.  
 1893 Merrell, Charles G .....Care of Wm. S. Merrell Chem. Co., Cincinnati, O.  
 1900 Merriam, Henry F.....Summit, N. J.  
 1892 Merrill, N. Fred .....Univ. of Vt., Burlington, Vt.  
 1898 Metcalf, W. V .....Northfield, Minn.  
 1892 Mew, W. M .....Lab. Army Med. Museum, Washington, D. C.  
 1900 Meyer, Gustave M .....59 E. 77th St., N. Y. City.  
 1899 Meyer, Max .....157 W. 103d St., N. Y. City.  
 1894 Michaelis, Gustavus.....541 Western Ave., Albany, N. Y.  
 1897 Michaelis, Theodore .....Care of Western Sugar Ref., Potrero, San Francisco, Cal.  
 1895 Miles, George W., Jr.....7 Exchange Pl., Boston, Mass.  
 1898 Miller, Alfred S .....Univ. of Idaho, Moscow, Idaho.  
 1899 Miller, Armand R.....808 Euclid Ave., Kansas City, Mo.  
 1895 Miller, Edmund H.....Columbia Univ., N. Y. City.  
 1899 Miller, Frank W.....Talladega, Ala.  
 1897 Miller, H. K.....Lake City, Fla.  
 1897 Miller, Harry East.....1015 Chestnut St., Oakland, Cal.  
 1895 Miller, Hugh L.....24 Broad St., Charleston, S. C.  
 1891 Miller, J. A.....255 Ellicott St., Buffalo, N. Y.  
 1897 Miller, P. Schuyler.....Mt. Prospect Lab., Flatbush Ave., Brooklyn, N. Y.  
 1895 Miller, Stephen C .....1235 New York Ave., N. W., Washington, D. C.  
 1898 Miller, W. Lash .....100 St. Vincent St., Toronto, Canada.  
 1900 Mills, James E.....Chapel Hill, N. C.  
 1893 Mills, Joseph S .....Central High School, Washington, D. C.  
 1897 Millwood, James P.....177 Spencer St., Brooklyn, N. Y.  
 1894 Miner, Harland S .....Care of Welsbach Light Co., Gloucester City, N. J.  
 1894 Mitchell, Andrew S .....220 Greenbush St., Milwaukee, Wis.  
 1897 Mittenzwey, Otto .....Care of Fitzgerald Bros., Troy, N. Y.  
 1895 Mixer, Chas. T .....Joplin, Mo.

- 1900 Mixter, Wm. G ..... Sheffield Scientific School, New Haven,  
Conn.
- 1895 Moale, Philip R ..... 100 Merrimon Ave., Asheville, N. C.
- 1898 Moat, C. P ..... 70 Middle St., Portsmouth, N. H.
- 1900 Moechel, Jean R ..... 710 Wyandotte St., Kansas City, Mo.
- 1898 Mommers, Richard ..... The Glucose Sugar Ref. Co., Rockford  
Lab., Rockford, Ill.
- 1898 Moody, Herbert R ..... 159 W. 105th St., N. Y. City.
- 1897 Mooers, C. A ..... Expt. Sta., Knoxville, Tenn.
- 1898 Moore, Byron L ..... 45th St. & Centre Ave., Chicago, Ill.
- 1900 Moore, F. J ..... Mass. Inst. Tech., Boston, Mass.
- 1898 Moore, George D ..... 21 Catharine St., Worcester, Mass.
- 1900 Moore, Hugh K ..... West Paris, Me.
- 1899 Moore, Russell W ..... Appraiser's Stores, Washington and Chris-  
topher Sts., N. Y. City.
- 1898 Moran, George A ..... 333 Haverhill St., Lawrence, Mass.
- 1895 Morgan, J. Livingston R .... 47 Bayard St., New Brunswick, N. J.
- 1885 Morgan, T. M ..... Longue Pointe, Hochilaga County, Can-  
ada.
- 1900 Mork, Harry S ..... 21 Wabeno St., Roxbury, Mass.
- 1894 Morse, Fred. W ..... Lock Box 30, Durham, N. H.
- 1899 Morton, Cora ..... Norwood, Cincinnati, O.
- 1876 Morton, Henry ..... Stevens Institute, Hoboken, N. J.
- 1899 Motion, John ..... Care of John Ellis & Co., Edgewater,  
N. J.
- 1894 Moulton, Charles W ..... 19 Virginia Ave., Poughkeepsie, N. Y.
- 1894 Moyer, J. Bird ..... Univ. of Pa., Philadelphia, Pa.
- 1899 Mudge, Charles W ..... Agr. Expt. Sta., Geneva, N. Y.
- 1898 Mulliken, Samuel P ..... Mass. Inst. Tech., Boston, Mass.
- 1892 Mumper, W. N ..... 823 W. State St., Trenton, N. J.
- 1890 Muñoz, L. E ..... Ingenio "Las Canas," Alfonso XII, Cuba.
- 1876 **MUNROE, C. E.** ..... Columbian Univ., Washington, D. C.
- 1881 Munsell, C. E ..... 110 Horatio St., N. Y. City.
- 1900 Munson, L. S ..... Dept. of Agr., Washington, D. C.
- 1895 Murray, C. B ..... Braddock, Pa.
- 1897 Murrill, Paul I ..... Hickory, N. C.
- 1896 Myers, H. Ely ..... Lincoln Foundry Co., 60th and Butler  
Sts., Pittsburg, Pa.
- 1893 Myers, J. A ..... Anderson Building, 12-16 John St., N. Y.  
City.
- 1894 Myers, Wm. S ..... Rutgers College, 15 Union St., New  
Brunswick, N. J.
- 1900 **NATHAN, Albert F., Jr.** .... 603 Mumford Court, Kansas City, Mo.
- 1895 Neher, F ..... Princeton, N. J.
- 1898 Neidich, Samuel A ..... 1041 Drexel Building, Philadelphia, Pa.

- 1900 Neilson, Thomas.....Mowry Mine, Crittenden, Ariz.  
1899 Neiman, Howard S.....8 E. 97th St., N. Y. City.  
1900 Neish, Arthur C .....308 University Ave., Kingston, Ontario.  
1895 Nelson, E. K .....4526 Oakenwald Ave., Chicago, Ill.  
1900 Nelson, N .....9057 Commercial Ave., So. Chicago, Ill.  
1896 Neustadt, George M. S .....234 E. 27th St., N. Y. City.  
1897 Newell, Lyman C .....State Normal School, Lowell, Mass.  
1892 Newman, H. E .....2543 Moorman Ave., Cincinnati, O.  
1899 Newman, Jacob W .....Empire Hotel, N. Y. City.  
1900 Newton, Elmer S .....Western High School, Washington, D. C.  
1898 Nicholls, George A.....Deadwood, S. D.  
1899 Nichols, Herbert T.....Care of Puertocitos Copper Co., Bisbee,  
Ariz.  
1876 Nichols, W. H .....32 Liberty St., N. Y. City.  
1895 Nicholson, Edward E .....Univ. of Minn., Minneapolis, Minn.  
1891 Nicholson, H. H.....Univ. of Nebraska, Lincoln, Neb.  
1893 Nickel, Herman L .....Care of The N. K. Fairbank Co., St. Louis,  
Mo.  
1876 Niese, H. E.....Matthiessen & Wiechers, Jersey City,  
N. J.  
1900 Nikaido, Y .....2375 O St., Lincoln, Nebr.  
1897 Nishkian, P. F.....Care of Armour Packing Co., Kansas  
City, Mo.  
1900 Norman, Geo. M.....Tenn. C. I. and R. Co., Birmingham, Ala.  
1898 Norris, James F.....Mass. Inst. Tech., Boston, Mass.  
1900 Norris, Robert S .....Union Sugar Co., Santa Maria, Cal.  
1900 Norton, Alice P.....47 Hancock St., Auburndale, Mass.  
1891 Norton, T. H .....Univ. of Cincinnati, Cincinnati, O.  
1895 Noyes, Arthur A .....Mass. Inst. Tech., Boston, Mass.  
1893 Noyes, W. A.....Rose Poly. Inst., Terre Haute, Ind.  
1898 Nye, Walter B .....Cumberland Mfg. Co., Boston, Mass.  
1897 OBERHOLTZER, Vickers.1905 Tioga St., Philadelphia, Pa.  
1894 Ogilvy, David J.....1403 State Ave., Cincinnati, O.  
1899 Oglesby, William R .....212 E. Broad St., Chester, Pa.  
1898 Olney, Louis A.....Lowell Textile School, Lowell, Mass.  
1898 Olsson, Gustaf.....10 Hampshire St., Everett, Mass.  
1895 O'Neill, Edmund.....Univ. of California, Berkeley, Cal.  
1898 O'Regan, Daniel F.....Worcester Poly. Inst., Worcester, Mass.  
1877 Orth, A.....194 Fulton St., N. Y. City.  
1893 Osborne, Thomas B .....Box 485, New Haven, Conn.  
1893 PALMER, Arthur W .....Univ. of Ill., Champaign, Ill.  
1897 Palmer, Charles S.....Univ. of Colorado, Boulder, Colo.  
1895 Palmer, Chase .....1406 Garvin Pl., Louisville, Ky.  
1891 Parker, C. E.....150 Alden St., Orange, N. J.  
1900 Parker, C. LeRoy .....Patent Office, Washington, D. C.

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- 1883 Peters, Andrew.....Hulett's Landing, Washington Co., N. Y.  
 1895 Peyton, Wm. C.....Peyton Chem. Wks., Mutual Life Bldg.,  
 San Francisco, Cal.  
 1900 Phalen, Wm. C.....Socorro, N. M.  
 1898 Phelan, J. W.....Mass. Inst. Tech., Boston, Mass.  
 1900 Phelps, Isaac K.....130 Howe St., New Haven, Conn.  
 1894 Phillips, Francis C.....P. O. Box 126, Allegheny, Pa.  
 1897 Phillips, Wm. B.....213 Ninth St., Pittsburg, Pa.  
 1891 Phillips, Wm. D.....128 Pearl St., N. Y. City.  
 1899 Phinney, John 1.....24 Langdon St., Cambridge, Mass.  
 1897 Pickel, J. M.....W. Raleigh, N. C.  
 1896 Pickering, Oscar W.....52 Clifton Park, Melrose Highlands,  
 Mass.  
 1895 Pickert, Leo W.....Amer. Sug. Ref. Co., Granite St., Bos-  
 ton, Mass.  
 1898 Pierce, Edward W.....109 N. Water St., Philadelphia, Pa.  
 1898 Pierson, Willett C.....7 St. James Pl., Brooklyn, N. Y.  
 1896 Pilhashy, Benjamin M.....906-910 Sycamore St., Cincinnati, O.  
 1897 Pinkerton, David J.....17 Orbiston St., Motherwell, Scotland.  
 1898 Piper, Walter E.....Boston Rubber Shoe Co., Fells, Mass.  
 1890 Pitkin, Charles A.....Thayer Academy, South Braintree,  
 Mass.  
 1882 Pitkin, Lucius . . . . .138 Pearl St., N. Y. City.  
 1894 Pitman, John.....Augusta Arsenal, Augusta, Ga.  
 1896 Pitman, J. R.....Care of Lafin and Rand Powder Co.,  
 Pompton Lakes, N. J.  
 1893 Platt, Charles.....Hahnemann Med. College, Philadel-  
 phia, Pa.  
 1900 Platt, Elbert S.....Waterford, N. Y.  
 1888 Pomeroy, Charles T.....55 Broad St., Newark, N. J.  
 1898 Pond, F. J.....State College, Pa.  
 1892 Pond, G. G.....State College, Pa.  
 1898 Poole, Herman.....357 Canal St., N. Y. City.  
 1898 Pope, T. E.....Mass. Inst. Tech., Boston, Mass.  
 1898 Porter, Georgia.....Y. W. C. A., 18th and Arch Sts., Phila-  
 delphia, Pa.  
 1898 Portner, Edward G.....1104 Vermont Ave., Washington, D. C.  
 1900 Post, Frank I.....67 W. Alden St., Coldwater, Mich.,  
 1895 Potter, Charles A.....198 Waterman St., Providence, R. I.  
 1889 Potter, W. R.....100 Broad St., Providence, R. I.  
 1894 Power, Frederick B.....The Wellcome Research Lab., 6 King  
 St., Snow Hill, London, E. C.,  
 England.  
 1898 Pratt, Gilbert H.....Room 502, State House, Boston, Mass.  
 1898 Pratt, Joseph H.....Univ. of N. C., Chapel Hill, N. C.

- 1894 Prentiss, George N.....Care of Northwestern Iron Co., Mayville, Wis.
- 1876 Prescott, A. B .....Ann Arbor, Mich.
- 1898 Prescott, Samuel C.....Mass. Inst. Tech., Boston, Mass.
- 1898 Price, R. B.....Boston Woven Hose and Rubber Co., Cambridgeport, Mass.
- 1899 Priest, George W.....Watertown, Mass.
- 1877 Prochazka, G. A.....138 W. 13th St., N. Y. City.
- 1897 Prochazka, John.....15 E. 12th St., N. Y. City.
- 1895 Proctor, Richard W .....Care of the Wm. S. Merrell Chem. Co., Cincinnati, O.
- 1893 Provine, J. W .....Miss. College, Clinton, Miss.
- 1893 Puckner, W. A .....73 Wells St., Chicago, Ill.
- 1898 Pugh, Achilles H., Jr.....Madison Road, Cincinnati, O.
- 1899 Pullman, F. Cooper .....238 S. 3rd St., Philadelphia, Pa.
- 1898 QUINAN, Kenneth B .....Care of Cal. Powder Works, Pinole, Cal.
- 1891 Quinan, W. R.....Guardian Building, Cape Town, S. Africa.
- 1898 RANDALL, N. M.....Md. Steel Co., Sparrows Point, Md.
- 1894 Rawling, Charles Q .....403 Peabody Building, Wheeling, W. Va.
- 1895 Redding, Allen C .....Golconda Mine, Sumpter, Oregon.
- 1895 Redding, Clifford R .....Index, Snohomick Co., Wash.
- 1898 Redpath, Léon W .....620 Atlantic Ave., Boston, Mass.
- 1887 Redwood, Boverton.....4 Bishopgate St., Within, London, E. C., England.
- 1893 Reese, Charles L .....N. J. Zinc Co., Newark, N. J.
- 1900 Reid, E. Emmet.....Coll. of Charleston, Charleston, S. C.
- 1897 Reinus, Bernhard .....Paterson Chem. Works, First Ave., Paterson, N. J.
- 1900 Remington, Joseph P.....1832 Pine St., Philadelphia, Pa.
- 1898 Remsen, Ira.....Johns Hopkins Univ., Baltimore, Md.
- 1897 Reuter, L. H .....Mercks Building, N. Y. City.
- 1896 Rhodes, Edward .....Oaklands, Frodsham, Cheshire, Eng.
- 1887 Rice, Charles .....Bellevue Hospital, N. Y. City.
- 1893 Richards, Edgar.....341 W. 88th St., N. Y. City.
- 1898 Richards, Ellen H.....Mass. Inst. Tech., Boston, Mass.
- 1900 Richards, Joseph .....1802 Catherine St., Philadelphia, Pa.
- 1893 Richards, Joseph W .....Lehigh Univ., Bethlehem, Pa.
- 1898 Richards, Robert H.....Mass. Inst. Tech., Boston, Mass.
- 1898 Richards, Theodore W.....44 Shepard St., Cambridge, Mass.
- 1897 Richardson, Clifford.....Director N. Y. Testing Lab., Long Island City, N. Y.
- 1895 Richardson, George M.....Stanford Univ., Cal.
- 1876 Ricketts, P. de P.....Columbia Univ., N. Y. City.
- 1898 Riddell, D. F .....Waverly, Nebr.
- 1898 Riederer, Emil J .....Care of Hercules Powder Co., Ashburn, Mo.

- 1891 Riggs, G. W.....Summit, N. J.  
1894 Riggs, Louis W .....Cornell Univ. Med. College, 414 E. 26th  
St., N. Y. City.  
1895 Riggs, Robert B.....35 Forest St., Hartford, Conn.  
1899 Ripley, Philip F .....Andover, Mass.  
1899 Rippetoe, J. J .....Vallejo, Cal.  
1900 Rising, Herbert R.....208 Water St., Johnstown, Pa.  
1893 Rising, W. B .....Univ. of Cal., Berkeley, Cal.  
1899 Ritchey, J. C.....Nat. Steel Co., Mingo Junction, O.  
1897 Ritchey, J. Warren.....701 Baymiller St., Cincinnati, O.  
1895 Robbins, Wm. K .....Amoskeag Mills, Manchester, N. H.  
1898 Roberts, Charles C.....223 Sharpless St., West Chester, Pa.  
1898 Roberts, Charlotte F .....Wellesley College, Wellesley, Mass.  
1899 Roberts, W. H.....City Hall, Minneapolis, Minn.  
1899 Robertson, Benjamin F.....Clemson College, S. C.  
1893 Robertson, Wm .....P. O. Drawer D, Charleston, S. C.  
1894 Robinson, Wm. S .....1112 Dodge St., Omaha, Neb.  
1894 Roeser, Frederick .....240 W. 130th St., N. Y. City.  
1899 Rogers, Allen .....Univ. of Maine, Orono, Me.  
1893 Rolfe, George W.....405 Broadway, Cambridge, Mass.  
1898 Root, William L.....St. John's School, Manlius, N. Y.  
1900 Root, William W.....186 Eugenie St., Chicago, Ill.  
1893 Rosell, C. A. O .....268 W. Broadway, N. Y. City.  
1899 Rosenberg, Martin A .....27 Lambert Ave., Roxbury, Mass.  
1895 Rosengarten, George D.....1700 Fitzwater St., Philadelphia, Pa.  
1900 Rosentwist, Birger G. A ....Fessenden St., Jamaica Plain, Boston,  
Mass.  
1892 Ross, B. B.....State Chemist, Auburn, Ala.  
1900 Ross, Herbert W.....1070 16th St., Oakland, Cal.  
1896 Rossi, Auguste J.....35 Broadway, N. Y. City.  
1897 Rowland, Wm. L.....4800 Chester Ave., Philadelphia, Pa.  
1900 Rudnick, Paul F. A.....3701 S. Lincoln St., Chicago, Ill.  
1893 Runyan, E. G.....Dept. of Agr., Washington, D. C.  
1898 Russell, L. Kimball.....Mass. Inst. Tech., Boston, Mass.  
1893 SAARBACH, Ludwig .....23 William St., N. Y. City.  
1886 Sabin, A. H.....Box 85, Long Island City, N. Y.  
1893 Sadtler, Samuel P.....1042 Drexel Building, Philadelphia, Pa.  
1899 Sadtler, Samuel S .....336 Franklin St., Germantown, Phila-  
delphia, Pa.  
1894 Saltar, J. Coleman.....Pemberton, N. J.  
1895 Sanborn, E. R.....Sharon, Pa.  
1894 Sanders, C. N .....Ponce de Leon Hotel, Roanoke, Va.  
1893 Sanderson, John.....Box 84, Middlesborough, Ky.  
1900 Sandford, Wm. E.....Kewanee, Ill.  
1900 Sanger, Charles R.....Chem. Lab., Harvard College, Cam-  
bridge, Mass.



- 1896 Sargent, Charles L ..... Peace Dale, R. I.  
 1894 Sargent, George W ..... Carpenter Steel Co., Reading, Pa.  
 1899 Sarles, Edgar H ..... Ill. Chem. Co., Chicago Heights, Ill.  
 1893 Sauer, Ewald ..... Wilhelm Strasse 50, Berlin, Germany.  
 1899 Saunders, A. P ..... Cornell Univ., Ithaca, N. Y.  
 1891 Saunders, Walter M ..... 20 Dewey St., Olneyville, R. I.  
 1898 Sawyer, Harris E ..... 37 Gates St., South Boston, Mass.  
 1897 Sawyer, Harry B ..... Broad and Commercial Sts., Bath, Me.  
 1900 Schaak, Milton F ..... 108 Penn St., Brooklyn, N. Y.  
 1894 Schaeffer, Henri ..... Manchester Mills, Manchester, N. H.  
 1897 Schaffer, H. A ..... 347 Broadhead St., Easton, Pa.  
 1894 Schanche, Herman G ..... 3401 Gray's Ferry Road, Philadelphia, Pa.  
 1891 Schedler, Robert W ..... 405 4th St., Brooklyn, N. Y.  
 1898 Scherr, E. W., Jr ..... 2067 7th Ave., N. Y. City.  
 1894 Schiedt, Richard C ..... 526 W. James St., Lancaster, Pa.  
 1891 Schieffelin, W. J ..... 170 William St., N. Y. City.  
 1894 Schiller, Louis J ..... Care of Arbuckle Bros., Foot of Pearl St.,  
 Brooklyn, N. Y.  
 1894 Schimpf, Henry W ..... 372 W. 35th St., N. Y. City.  
 1898 Schleicher, F. J ..... 38 W. 10th St., Long Island City, N. Y.  
 1899 Schlichting, Emil ..... 103 N. Front St., Philadelphia, Pa.  
 1895 Schloss, Joseph A ..... Care of La Gran Fundicion Nacional  
 Mexicana, Monterey, Mexico.  
 1894 Schmidt, Louis ..... 215 E. 4th St., Cincinnati, O.  
 1900 Schnierwind, F ..... United Coke and Gas Co., 36 Wall St.,  
 N. Y. City.  
 1899 Schober, W. B ..... Lehigh Univ., So. Bethlehem, Pa.  
 1899 Schoch, Eugene P ..... Kent Chem. Lab., Univ. of Chicago,  
 Chicago, Ill.  
 1896 Schoen, Joseph ..... Care of Standard Syrup Ref. Co., 12 S.  
 Commercial St., St. Louis, Nev.  
 1900 Schoonmaker, H ..... 120 N. Main St., Los Angeles, Cal.  
 1895 Schroeder, Edward ..... 221 Pearl St., N. Y. City.  
 1886 Schüpphaus, R. C ..... 174 Broadway, N. Y. City.  
 1899 Schuyler, Erwin H ..... High School, Watertown, N. Y.  
 1892 Schweitzer, Hugo ..... 427 W. 117th St., N. Y. City.  
 1894 Scovell, M. A ..... Agr. Expt. Sta., Lexington, Ky.  
 1898 Scudder, Heyward ..... Mass. Inst. Tech., Boston, Mass.  
 1896 Seal, Alfred N ..... 405 Wister St., Germantown, Philadel-  
 phia, Pa.  
 1890 Seaman, Wm. H ..... 1424 11th St., Washington, D. C.  
 1894 Seamon, Wm. H ..... Box 97, El Paso, Texas.  
 1900 Sears, Frederick E ..... St. Paul's School, Concord, N. H.  
 1897 Sedding, George H. P ..... Care of Florida Syndicate, Jacksonville,  
 Fla.  
 1887 Seely, Henry Martyn ..... 3 South St., Middlebury, Vt.

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|------|-------------------------|---|
| 1890 | Seher, August           | 110 Montclair Ave., Newark, N. J.   |
| 1898 | Seidensticker, Lewis J. | Mass. Inst. Tech., Boston, Mass.  |
| 1894 | Seldner, Rudolph        | 217 Jefferson Ave., Brooklyn, N. Y.                                       |
| 1895 | Semans, Wm. O           | Ohio Wesleyan Univ., Delaware, O.   |
| 1894 | Share, Wm. W.           | 331 McDonough St., Brooklyn, N. Y.  |
| 1898 | Sharples, Philip P      | 13 Broad St., Boston, Mass.   |
| 1876 | Sharples, S. P          | 13 Broad St., Boston, Mass.   |
| 1895 | Sharwood, Wm. J.        | Care of Montana Mining Co., Ltd., Marysville, Lewis and Clarke Co., Mont. |
| 1897 | Shattuck, A. F.         | Solvay Process Co., Detroit, Mich.  |
| 1895 | Shaw, G. W              | Corvallis, Ore.   |
| 1899 | Shaw, H. I.             | Gilt Edge, Mont.  |
| 1896 | Shaw, Wm. T             | Bozeman, Mont.  |
| 1895 | Shepherd, Frank I.      | Univ. of Cincinnati, Cincinnati, O.                                       |
| 1898 | Sherman, G. W.          | Room 509, Exchange Bldg., 53 State St., Boston, Mass.                     |
| 1894 | Sherman, H. C           | Columbia University, N. Y. City.  |
| 1895 | Sherrard, Charles C.    | 121 20th St., Detroit, Mich.  |
| 1893 | Shimer, P. W.           | Easton, Pa.   |
| 1894 | Shinn, Owen Louis.      | Univ. of Pa., Philadelphia, Pa.   |
| 1898 | Shiver, Frank S.        | Clemson College, S. C.  |
| 1893 | Shorey, Edmund C.       | Box 360, Honolulu, H. I., U. S. A.  |
| 1894 | Shuler, D. P.           | Sudbury, Ont.   |
| 1894 | Shutt, Frank T.         | Ottawa, Canada.   |
| 1900 | Shuttleworth, Arthur E. | Guelph, Ontario.  |
| 1894 | Sidener, C. F           | Univ. of Minn., Minneapolis, Minn.  |
| 1894 | Sieker, Ferdinand A.    | 524 Bloomfield St., Hoboken, N. J.  |
| 1898 | Simmons, Ward W.        | Box 565, Johns Hopkins Univ., Baltimore, Md.                              |
| 1887 | Simon, S. E             | Belleville, N. J.   |
| 1876 | Simon, Wm               | 1348 Block St., Baltimore, Md.  |
| 1898 | Simons, Frank D         | "The Montrose Flats," 1115 9th St., Washington, D. C.                     |
| 1893 | Simonson, W             | 102 W. 9th St., Cincinnati, O.  |
| 1894 | Sims, Clough W          | 1706 Polk Ave., Houston, Tex.   |
| 1899 | Skinner, Hervey J       | General Chem. Co., Moro Phillips Works, Camden, N. J.                     |
| 1896 | Skinner, Wm. W.         | College Park, Md.   |
| 1896 | Slagle, Robert L.       | Rapid City, S. D.   |
| 1900 | Sloane, T O'Connor.     | 39 Wall St., N. Y. City.  |
| 1896 | Slosson, E. E.          | Univ. of Wyoming, Laramie, Wyo.   |
| 1898 | Small, Fritz H.         | Care of Graton and Knight Mfg. Co., Worcester, Mass.                      |
| 1891 | Smith, Albert L.        | 6531 Union Ave., Englewood, Ill.  |
| 1898 | Smith, Albert W.        | 1101 E. Madison Ave., Cleveland, O.                                       |
| 1898 | Smith, Arthur C         | Waltham, Mass.  |

- 1899 Smith, E. A ..... Anaconda, Mont.  
1893 Smith, Edgar F ..... Univ. of Pa., Philadelphia, Pa.  
1893 Smith, Edward L ..... 10 Lowell St., Worcester, Mass.  
1897 Smith, Erastus G ..... Beloit, Wis.  
1894 Smith, Ernest Ellsworth ..... 262 5th Ave., N. Y. City.  
1897 Smith, F. Warren ..... Care of Cal. Powder Works, Pinole, Cal.  
1898 Smith, Frederick J ..... Box 46, Elizabeth, N. J.  
1894 Smith, Harry E ..... 29 31st St., Milwaukee, Wis.  
1894 Smith, Herbert E ..... Yale Med. School, New Haven, Conn.  
1898 Smith, H. Monmouth ..... Univ. of Syracuse, Syracuse, N. Y.  
1898 Smith, Horace T ..... E. Bridgewater, Mass.  
1895 Smith, J. D. Audley ..... Care of Ariz. Copper Co., Ltd., Clifton,  
Ariz.  
1898 Smith, John W ..... Mass. Inst. Tech., Boston, Mass.  
1894 Smith, Walter E ..... 47 Jenkins St., Providence, R. I.  
1897 Smith, Warren R ..... Lewis Institute, Chicago, Ill.  
1900 Smither, F. W ..... Mount Pleasant, Tenn.  
1895 Smolt, F. O ..... 308 W. Broadway, Butte, Mont.  
1895 Smoot, Albert M ..... 260 W. Grand St., Elizabeth, N. J.  
1897 Smyth, Geo. A ..... 120 S. Grove Ave., Oak Park, Ill.  
1891 Snyder, Harry ..... Expt. Sta., St. Anthony Park, Minn.  
1899 Snyder, O. J ..... Rooms 515-519, Stephen Girard Bldg.,  
Philadelphia, Pa.  
1898 Snyder, Wm. H ..... Worcester Academy, Worcester, Mass.  
1897 Sohon, M. D ..... Mixed High School, N. Y. City.  
1898 Somermeier, E. E ..... Ohio State Univ., Columbus, O.  
1900 Soper, George A ..... 29 Broadway, N. Y. City.  
1894 Souther, Henry ..... 440 Capitol Ave., Hartford, Conn.  
1899 Sovereign, Clarence L ..... Glucose Sugar Ref. Co., Rockford, Ill.  
1898 Spencer, G. Carl ..... 2 Ames Pl., Lowell, Mass.  
1893 Spencer, G. L ..... Dept. of Agr., Washington, D. C.  
1893 Speyers, C. L ..... Rutgers College, New Brunswick, N. J.  
1898 Spieler, A. J ..... The Will and Baumer Co., Syracuse,  
N. Y.  
1890 Springer, Alfred ..... 312 E. 2nd St., Cincinnati, O.  
1877 Squibb, E. R ..... 36 Doughty St., Brooklyn, N. Y.  
1896 Stahl, Karl F ..... 57th St. and A. V. Ry., Pittsburg, Pa.  
1898 Stantial, F. G ..... Cochrane Chem. Co., Everett, Mass.  
1894 Starke, Frederick W ..... 1853 N. 28th St., Philadelphia, Pa.  
1887 Starr, H. F ..... 142 4th Ave., Newark, N. J.  
1900 Starz, Emil ..... 204 N. Rodney St., Helena, Mont.  
1900 Stead, J. E ..... Laboratory and Assay Office, Queen's  
Terrace, Middlesbrough, England.  
1892 Stearns, J. B ..... Univ. of Vermont, Burlington, Vt.  
1896 Stearns, T. C ..... 44 Montgomery St., Jersey City, N. J.  
1879 Stebbins, James H., Jr ..... 80 Madison Ave., N. Y. City.

- 1898 Steel, Frederick W.....Care of Cuming Smith & Co., Ltd.,  
Yarraville, Melbourne, Aus.
- 1893 Steiger, George .....1361 Yale St., N. W., Washington, D. C.
- 1894 Stephens, Henry M .....Dickinson College, Carlisle, Pa.
- 1899 Stephens, W. B.....Stephens & Bro., Marshall Ave., Cincinnati, O.
- 1898 Stern, David.....112 Garfield Pl., Cincinnati, O.
- 1898 Stern, Heinrich .....1338 Lexington Ave., N. Y. City.
- 1891 Sternberg, L.....34 Louisen Strasse, Munich, Germany.
- 1898 Stetson, Frank O.....U. S. Weather Bureau, Washington,  
D. C.
- 1900 Stevens, Alviso B.....915 Oakland Ave., Ann Arbor, Mich.
- 1898 Stevens, Edward K.....8 Washington Sq., Newport, R. I.
- 1899 Sticht, Gustave A. H.....Care of Tartar Chem. Co., Jersey City,  
N. J.
- 1892 Stiles, W. M .....Care of Edward Smith Co., Box 85, Long  
Island City, N. Y.
- 1897 Stillman, John M .....Stanford Univ., Cal.
- 1890 Stillman, Thomas B .....Stevens Institute, Hoboken, N. J.
- 1876 Stillwell, C. M.....55 Fulton St., N. Y. City.
- 1893 Stillwell, J. S .....18 Great Windmill St., Piccadilly Cir-  
cus, London, W., England.
- 1896 Stocker, John H.....214 Hancock St., Brooklyn, N. Y.
- 1895 Stoddard, John T .....57 Crescent St., Northampton, Mass.
- 1893 Stokes, Henry N .....U. S. Geol. Surv., Washington, D. C.
- 1894 Stone, George C.....115 Broadway, N. Y. City.
- 1894 Stone, Winthrop E.....Purdue Univ., Lafayette, Ind.
- 1899 Street, John Phillips.....N. J. Agr. Expt. Station, New Bruns-  
wick, N. J.
- 1897 Stürcke, H. E .....284 Pearl St., N. Y. City.
- 1900 Sullivan, E. C.....331 Packard St., Ann Arbor, Mich.
- 1898 Sullivan, J. M.....Centenary College, Jackson, La.
- 1896 Summers, Bertrand S .....Care of Western Electric Co., Chicago,  
Ill.
- 1900 Sundstrom, Carl .....Solvay Process Co., Detroit, Mich.
- 1900 Sundstrom, Karl J.....Trenton, Wayne Co., Mich.
- 1898 Suter, Frank .....Eastern High School, Washington, D. C.
- 1898 Sutro, H. H.....60 W. 49th St., N. Y. City.
- 1899 Swan, Clifford M .....91 Babcock St., Brookline, Mass.
- 1894 Swan, J. N .....Monmouth, Ill.
- 1894 Sweetser, R. C .....Greendale, Mass.
- 1895 Swenson, M .....944 Monadnock Block, Chicago, Ill.
- 1895 Swett, Charles E.....171 Pleasant St., Providence, R. I.
- 1896 Sy, Albert P.....24 High St., Buffalo, N. Y.
- 1900 Syme, Wm. A .....North and Person Sts., Raleigh, N. C.
- 1897 TAGGART, Walter T.....730 N. 20th St., Philadelphia, Pa.

- |      |                              |  |
|------|------------------------------|--|
| 1897 | Takamine, Jokichi .....      | 475 Central Park, West, N. Y. City.                          |
| 1894 | Talbot, Henry P .....        | Mass. Inst. Tech., Boston, Mass.                             |
| 1893 | Tassin, Wirt.....            | U. S. Nat. Museum, Washington, D. C.                         |
| 1894 | Taylor, Duncan W.....        | Colgate & Co., Jersey City, N. J.                            |
| 1900 | Taylor, H. W.....            | 204 Carondelet St., New Orleans, La.                         |
| 1898 | Taylor, Sherburne F .....    | 3134 Boulevard, N. Y. City.                                  |
| 1900 | Taylor, Thomas M .....       | Oberlin, O.  |
| 1891 | Teeter, C. W.....            | 211 Hamilton St., Peoria, Ill.                               |
| 1894 | Teller, G. L .....           | Fayetteville, Ark.   |
| 1896 | Tennille, Geo. F .....       | Care of Southern Cotton Oil Co., Savan-<br>nah, Ga.          |
| 1876 | Terne, Bruno .....           | The Ammonia Salts Mfg. Co., Pekin, Ill.                      |
| 1898 | Terry, John P.....           | Box 51, Anaconda, Mont.                                      |
| 1890 | Textor, Oscar.....           | 158 Superior St., Cleveland, O.                              |
| 1896 | Thatcher, Charles J .....    | Care of B. T. Babbitt, 82 Washington St.,<br>N. Y. City.     |
| 1897 | Thatcher, R. W.....          | Agr. Expt. Sta., Lincoln, Neb.                               |
| 1898 | Thayer, Fred. L .....        | Rumford Chem. Wks., Providence, R. I.                        |
| 1898 | Thigpen, John H .....        | Keachie, La.   |
| 1894 | Thomas, N. Wiley .....       | Rooms 330-332, City Hall, Philadelphia,<br>Pa.               |
| 1898 | Thomas, W. H., Jr.....       | Colonial Bleaching and Printing Co., St.<br>Henry, Montreal. |
| 1896 | Thomas, William S .....      | Belt, Cascade Co., Mont.                                     |
| 1896 | Thompson, Firman.....        | Sugar Expt. Station, Honolulu, H. I.,<br>U. S. A.            |
| 1899 | Thompson, Milton S .....     | Box 1, Newburyport, Mass.                                    |
| 1895 | Thomson, Elihu .....         | Swampscott, Mass.  |
| 1898 | Thomson, Mary J.....         | 119 W. Grand St., Elizabeth, N. J.                           |
| 1895 | Thorburn, A. D.....          | Room 200, 100 State St., Chicago, Ill.                       |
| 1900 | Thorne, Ernest E. H.....     | Care of H. E. Thorne & Son, Barbadoes,<br>W. I.              |
| 1897 | Thorp, Frank H .....         | Mass. Inst. Tech., Boston, Mass.                             |
| 1898 | Thorpe, Edward E .....       | 711 Boylston St., Boston, Mass.                              |
| 1898 | Thrasher, Edward C .....     | Newport, Vt.   |
| 1900 | Thurlow, Nathaniel .....     | 55 New St., Newark, N. J.                                    |
| 1898 | Thurnauer, Gustav.....       | Aurora Metal Co., Aurora, Ill.                               |
| 1894 | Thurston, Azor .....         | Grand Rapids, Wood Co., O.                                   |
| 1897 | Tibbals, W. I .....          | 99 Cass St., Detroit, Mich.                                  |
| 1896 | Tiffany, W. C .....          | 214 Spruce St., N. Y. City.                                  |
| 1890 | Tobin, John J.....           | 18 White St., Newport, R. I.                                 |
| 1897 | Toch, M.....                 | 468-472 W. Broadway, N. Y. City.                             |
| 1895 | Todd, Albert M .....         | Kalamazoo, Mich.   |
| 1895 | Tompkins, Vreeland.....      | 533 Communipaw Ave., Jersey City, N. J.                      |
| 1898 | Torrey, Charles A., Jr ..... | 1015 S. 48th St., Philadelphia, Pa.                          |
| 1900 | Torrey, Henry A.....         | 75 S. Prospect St., Burlington, Vt.                          |

- 1894 Touceda, Enrique ..... Care of Troy Steel Co., Troy, N. Y.  
1899 Tower, Olin F ..... Adelbert College, Cleveland, O.  
1894 Townsend, Clinton P. .... U. S. Patent Office, Washington, D. C.  
1894 Traphagen, F. W. .... Bozeman, Mont.  
1893 Treat, Joseph A. .... Stuart, Iowa.  
1893 Trescot, T. C. .... Century Club, Washington, D. C.  
1899 Trotz, J. O. Emanuel. .... 20 Green Lane, Worcester, Mass.  
1899 Trowbridge, Miles L. ...., ... Care of Merck & Co., University and  
Clinton Pl., N. Y. City.  
1898 Trowbridge, Perry F. .... 226 Observatory St., Ann Arbor, Mich.  
1893 Trubek, Moses. .... 26 E. 104th St., N. Y. City.  
1900 Tucker, Charles W. .... 8 Grover St., Lynn, Mass.  
1893 Tucker, George P. .... Room 240, Patent Office, Washington,  
D. C.  
1895 Tucker, Samuel A. .... Havemeyer Hall, Columbia Univ., N. Y.  
City.  
1883 Tucker, W. G. .... Albany Medical College, Albany, N. Y.  
1899 Tuschka, Otto ..... Care of Seamon Lab., El Paso, Texas.  
1895 Tuthill, J. B. T. .... Salem Gas Light Co., Salem, Ore.  
1894 Tuttle, D. K. .... U. S. Mint, Philadelphia, Pa.  
1899 Tutwiler, C. C. .... 703 United Gas Building, Philadelphia,  
Pa.  
1892 Twitchell, E. .... Wyoming, O.  
1896 Tyrer, Thomas ..... Stirling Chem. Works, Stratford, London,  
E., England.  
1896 UHLIG, E. C. .... 229 E. 12th St., N. Y. City.  
1895 Ullmann, H. M. .... Lehigh Univ., South Bethlehem, Pa.  
1898 Underwood, G. R. .... Box 460, Peabody, Mass.  
1899 VAN BRUNT, Charles. .... 3617 Oak St., Kansas City, Mo.  
1897 Van Cleve, Carl E. .... 603 5th St., S. E., Minneapolis, Minn.  
1879 Vanderpoel, Frank. .... 153 Center St., Orange, N. J.  
1899 Van Dyck, Edwin M. .... Bureau Engraving and Printing, Wash-  
ington, D. C.  
1897 Van Gelder, Arthur P. .... Atlantic Dynamite Co., Rustic, N. J.  
1891 Van Gundy, C. P. .... Chief Chemist B. & O. R. R., Baltimore,  
Md.  
1894 Van Ingen, Dudley A. .... N. J. Zinc Co., Newark, N. J.  
1900 Van Riper, George B. .... Rutherford, N. J.  
1898 Van Slooten, William ..... 52 Sidney Pl., Brooklyn, N. Y.  
1900 Van Slyke, Lucius L. .... Agr. Expt. Station, Geneva, N. Y.  
1894 Veitch, F. P. .... College Park, Md.  
1894 Venable, F. P. .... Univ. of N. C., Chapel Hill, N. C.  
1896 Vinson, Albert E. .... Ohio State Univ., Columbus, O.  
1894 Volckening, Gustave J. .... 315 Quincy St., Brooklyn, N. Y.  
1883 Volney, C. W. .... 173 W. 81st St., N. Y. City.

- 1899 von Egloffstein, C.....714 Bushwick Ave., Brooklyn, N. Y.  
 1893 Von Herff, B.....German Kali Co., 93 Nassau St., N. Y.  
 City.  
 1894 Voorhees, Edward B .....New Brunswick, N. J.  
 1900 Voorhees, Gerald E .....Berwick, Pa.  
 1893 Voorhees, Louis A .....Box 290, New Brunswick, N. J.  
 1893 Voorhees, Samuel S .....N. Y. C. R. R., West Albany, N. Y.  
 1898 Vreeland, Cornelius D.....Care of Ill. Chem. Co., Chicago Heights,  
 Ill.  
 1898 Vulté, Hermann T .....Barnard College, N. Y. City.  
 1900 WACHTER, Leonard M...45 James St., Green Island, N. Y.  
 1893 Wade, E. M .....115½ N. Main St., Los Angeles, Cal.  
 1894 Wadman, Walter E .....102 Lord Ave., Bayonne, N. J.  
 1899 Wagner, Theodore B .....52 Walton Pl., Chicago, Ill.  
 1885 Wainwright, J. H .....159 Front St., N. Y. City.  
 1895 Wait, Charles E.....Univ. of Tenn., Knoxville, Tenn.  
 1898 Wakefield, Frank P .....4 Haskins Court, Malden, Mass.  
 1895 Wakeman, Alfred J .....Greenwich, Conn.  
 1893 Waldbott, Sigmund.....224 W. Court St., Cincinnati, O.  
 1878 Waldstein, M. E .....107 Murray St., N. Y. City.  
 1895 Walker, Henry V .....40 Clinton St., Brooklyn, N. Y.  
 1893 Walker, Percy H.....Ala. Cons. C. and I. Co., Gadsden, Ala.  
 1898 Walker, Wm. H .....Mass. Inst. Tech., Boston, Mass.  
 1891 Wallace, E. C .....Foot of W. 6th St., Long Island City, N.Y.  
 1894 Wallenstein, Florian .....Oranienburgerstrasse 28, Berlin, N.,  
 Germany.  
 1876 WALLER, ELWYN .....159 Front St., N. Y. City.  
 1898 Walls, Arthur W.....Care of Merrimac Chem. Co., North  
 Woburn, Mass.  
 1899 Ward, Delancey W.....247 Sanford Ave., Flushing, N. Y.  
 1893 Warder, Robert B .....Howard Univ., Washington, D. C.  
 1894 Wardman, George B.....2ª Ojocaliente num. 8, Apartado 24, Ag-  
 uascalientes, Mexico.  
 1899 Ware, Ezra J.....241 Belvidere Ave., Detroit, Mich.  
 1890 Washburn, J. H.....R. I. Coll. of A. and M. Arts, Kingston,  
 R. I.  
 1898 Wason, Robert S.....61-63 Chatham St., Boston, Mass.  
 1894 Waterman, Chauncey N .....134 50th St., Chicago, Ill.  
 1898 Watkins, Williard H .....87 Poplar St., Roslindale, Mass.  
 1898 Watson, Edward T.....172 E. Main St., Chillicothe, O.  
 1898 Watters, Leon L .....153 E. 56th St., N. Y. City.  
 1897 Weber, Everhard.....4277 Williamson Pl., Cumminville, Cin-  
 cinnati, O.  
 1876 Weber, H. A.....State Univ., Columbus, O.  
 1897 Weed, Henry T .....M. T. High School, Brooklyn, N. Y.

- 1894 Weems, J. B ..... Iowa Agr. Coll., Ames, Iowa.  
 1899 Weissmann, Fred. W. .... 221 Molitor St., Cincinnati, O.  
 1900 Weld, Fred C. .... Avery Chem. Co., Littleton, Mass.  
 1891 Welles, A. H. .... 635 Quincy Ave., Scranton, Pa.  
 1891 Wellington, Charles. .... 32 Amity St., Amherst, Mass.  
 1900 Wells, Allan ..... 213 S. St. Clair St., Pittsburg, Pa.  
 1895 Wells, Horace L. .... 57 Trumbull St., New Haven, Conn.  
 1898 Wells, James S. C. .... Columbia Univ., N. Y. City.  
 1899 Welt, Ida ..... 814 Lexington Ave., N. Y. City.  
 1895 Wentworth, W. V. .... Penobscot Chem. Fibre Co., Great Works,  
 Me.  
 1897 Werk, Louis ..... Westwood, Cincinnati, Ohio.  
 1897 Wessling, Hannah L. .... 549 Milton St., Cincinnati, O.  
 1891 Wesson, David ..... Box 458, Savannah, Ga.  
 1892 Westenfelder, B. D. .... Amer. Oak Leather Co., Cincinnati, O.  
 1893 Westessan, J. P. L. .... Navy Yard, Washington, D. C.  
 1898 Weston, David B. .... 42 Riverside St., Watertown, Mass.  
 1894 Weston, Robert Spurr ..... 14 Beacon St., Boston, Mass.  
 1899 Wetterstroem, Theodore D. ... Spring Grove Ave. and Cooper St., Cin-  
 cinnati, O.  
 1894 Wheeler, Edward J. .... 79 Chapel St., Albany, N. Y.  
 1890 Wheeler, H. J. .... Chemist R. I. Expt. Station, Kingston,  
 R. I.  
 1900 Wheeler, Henry L. .... Sheffield Chem. Lab., New Haven, Conn.  
 1900 Whipple, George C. .... Flatbush Ave. and Eastern Parkway,  
 Brooklyn, N. Y.  
 1898 Whitaker, DeBerniere ..... Spanish-American Iron Co., Santiago de  
 Cuba, Cuba.  
 1898 Whitaker, M. C. .... Columbia Univ., N. Y. City.  
 1895 White, Alfred H. .... 413 E. Liberty St., Ann Arbor, Mich.  
 1891 White, C. H. .... U. S. Naval Museum of Hygiene, Wash-  
 ington, D. C.  
 1898 White, G. Rantoul ..... Exeter Academy, Exeter, N. H.  
 1894 White, H. C. .... Univ. of Georgia, Athens, Ga.  
 1895 White, John ..... Box 675, Lincoln, Nebr.  
 1898 White, Laura B. .... 1 Copeland Pl., Roxbury, Mass.  
 1892 Whitehead, Cabell ..... Bureau of the Mint, Treas. Dept., Wash-  
 ington, D. C.  
 1895 Whitehead, R. L. .... Box 142, Mt. Washington, Md.  
 1894 Whitfield, J. Edward ..... 406 Locust St., Philadelphia, Pa.  
 1897 Whitney, Willis R. .... Mass. Inst. Tech., Boston, Mass.  
 1900 Whittier, Charles T. .... Provident Chem. Wks., St. Louis, Mo.  
 1894 Wiborg, F. B. .... The Ault & Wiborg Co., Box 844, Cin-  
 cinnati, O.  
 1893 Wickhorst, Max H. .... Care of C. B. & Q. Ry., Aurora, Ill.  
 1899 Wiechmann, F. G. .... 771 West End Ave., N. Y. City.



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1896	YATES, J. A.....	Ottawa Univ., Ottawa, Kansas.
1894	Yeates, W. S .....	State Geologist, Atlanta, Ga.
1898	Yeaton, Arthur C.....	Westbrook Seminary, Portland, Me.
1894	Yocum, John H.....	30 Ferry St., N. Y. City.
1876	Youmans, Wm. J.....	72 5th Ave., N. Y. City.
1892	Young, A. V. E.....	N. W. University, Evanston, Ill.
1898	Young, Stewart W.....	Stanford University, Cal.
1894	Yount, Clarence E.....	Columbia Hospital, 25th St. and Penn- sylvania Ave., N. W., Washington. D. C.
1900	ZIEGLER, J. Clayton.....	U. S. Naval Torpedo Station, Newport, R. I.
1899	Zimmele, H. B .....	53 S. Washington Sq., N. Y. City.
1893	Zimmer, Hermann W.....	Care of Wheeling Pottery Co., Wheeling, W. Va.
1892	Zinsser, Fred. G.....	Hastings-on-Hudson, N. Y.
Total.....		1546

# ASSOCIATES.

- 1899 **ALLEN**, Lucius E.....215 E. Liberty St., Ann Arbor, Mich.  
1895 Allison, Wm. O.....100 William St., N. Y. City.  
1898 Ames, George E.....119 Hall St., Lowell, Mass.  
1897 Anderson, Chas. A.....Litchfield, Minn.  
1898 Annison, Frederick G.....Hohokus, Bergen Co., N. J.  
1897 Armstrong, Theodore.....Care of Penna. Salt Mfg. Co., 115 Chest-  
nut St., Philadelphia, Pa.  
1891 Arnold, N. D.....Rumford Chem. Co., Providence, R. I.  
1898 Ashby, George J. M.....3716 Wabash Ave., Chicago, Ill.  
1898 Atteaux, F. E.....176 Purchase St., Boston, Mass.  
1897 **BAKER**, Dicia H.....Care of Presbyterian Hospital, W. 6th St.,  
Cincinnati, O.  
1900 Berghausen, Oscar.....644 Crown St., Walnut Hills, Cincin-  
nati, O.  
1900 Bloch, Jesse A.....Bloch Bros. Tobacco Co., Wheeling,  
W. Va.  
1894 Bradley, Edson .....45 Broadway, N. Y. City.  
1896 Brinton, C. S.....Box 1894, West Chester, Pa.  
1897 Bunker, Henry A.....158 6th Ave., Brooklyn, N. Y.  
1893 Burgess, Herbert S.....Box 1131, Providence, R. I.  
1900 Burke, Edmund.....Bozeman, Mont.  
1898 Butler, Paul.....Lowell, Mass.  
1899 Butler, Robert H.....406 E. Sandusky Ave., Bellefontaine, O.  
1898 Butler, Winthrop F.....79 Tudor St., Chelsea, Mass.  
1900 **CALVERT**, Joseph E.....Etna, Allegheny Co., Pa.  
1895 Church, Herbert Kenneth...112 Martien Hall, Lafayette College,  
Easton, Pa.  
1898 Clapp, Eugene H.....35 Federal St., Boston, Mass.  
1900 Clark, Clara.....201 N. Jackson St., Butte, Mont.  
1880 Cochrane, Hugh.....55 Kilby St., Boston, Mass.  
1899 Coffin, Edward F.....102 High St., Newburyport, Mass.  
1900 Condit, Louis C.....139 Lafayette Ave., Brooklyn, N. Y.  
1899 **DARKE**, Jesse M.....7 Oakville St., Lynn, Mass.  
1894 Davidson, Geo. H.....28 Woodbine St., Brooklyn, N. Y.  
1898 Dederick, Prescott K., Jr....Box 665, Albany, N. Y.  
1899 Driehaus, Irwin W.....Madisonville, O.  
1894 DuPont, Alexis I.....Wilmington, Del.  
1900 **ECCLES**, David C.....191 Dean St., Brooklyn, N. Y.  
1898 Ellis, Carleton.....195 Winchester St., Keene, N. H.

- 1898 Ellsworth, William.....16 Lafayette Ave., N. Y. City.
- 1898 **FERNANDEZ-CAVADA**, F Cienfuegos, Cuba.
- 1897 Finke, Albert H .....9th and Race Sts., Cincinnati, O.
- 1897 Finley, Norval H .....6638 Deary St., Pittsburg, Pa.
- 1899 Fite, Campbell C.....1 Madison Ave., N. Y. City.
- 1897 Foster, Albert D .....124 Charlotte Ave., Detroit, Mich.
- 1897 Fuller, R. Clinton .....Fuller Iron Works, Providence, R. I.
- 1898 **GAGNEBIN**, C. L.....140 Oliver St., Boston, Mass.
- 1900 Gearing, James H.....2111 Sidney St., Pittsburg, Pa.
- 1897 Germer, James W.....511 Lincoln Ave., Chicago, Ill.
- 1899 Goldstein, Harris .....228 Henry St., N. Y. City.
- 1900 Goodenough, Robert J .... .18 7th Ave., Brooklyn, N. Y.
- 1894 Goodridge, E. A .....Flushing, N. Y.
- 1898 **HALL**, Arthur W.....Ziegler Electric Co., 141 Franklin St.,  
Boston, Mass.
- 1894 Harrison, C. Leland.....35th St. and Gray's Ferry Road, Phila-  
delphia, Pa.
- 1897 Haslwanter, Chas .....904 Flushing Ave., Brooklyn, N. Y.
- 1899 Hawkins, C. C.....Flat 6, Cumberland Bldg., Avondale, Cin-  
cinnati, O.
- 1899 Hildreth, Edward T.....338 N. Main St., Los Angeles, Cal.
- 1898 Hobbs, Alexander F.....Merrimack Mfg. Co., Lowell, Mass.
- 1898 Holmes, V. Frank .....Mass. Inst. Tech., Boston, Mass.
- 1898 Howard, Alonzo P .....13 Pearl St., Boston, Mass.
- 1898 Howe, Chester A.....92 State St., Boston, Mass.
- 1898 Hubbard, G. C.....Tottenville, Staten Id., N. Y.
- 1891 Huntington, S. V. V .....69 E. 78th St., N. Y. City.
- 1899 **KEISER**, (Miss) Marshall..Hotel Avenel, Fort Thomas, Ky.
- 1899 Kendall, Arthur I.....338 Broadway, Somerville, Mass.
- 1900 Kiehn, Joseph F .....Nelson Morris & Co., U. S. Yards, Chi-  
cago, Ill.
- 1894 Kiessig, C. H .....4 Gold St., N. Y. City.
- 1899 Kinsley, Wm. J.....202 Broadway, N. Y. City.
- 1899 Knight, George W .....38 Rosseter St., Boston, Mass.
- 1876 **KUTTROFF, ADOLPH**.....128 Duane St., N. Y. City.
- 1894 **LANNING**, John G.....Horst, O.
- 1899 Loeser, Robert M .....Palo Alto, Cal.
- 1895 Louder, J. Willis.....411 Walnut St., Catasauqua, Pa.
- 1899 Lysle, Walter S .....223 Chartier St., Allegheny, Pa.
- 1891 **MAITLAND**, Alexander....45 Broadway, N. Y. City.
- 1893 Mallinckrodt, Edward .....Mallinckrodt Chem. Works, St. Louis,  
Mo.
- 1898 Marble, J. Russel .....Box 233, Worcester, Mass.

- 1899 Masury, John W ..... Centre Moriches, Long Island, N. Y.  
 1876 Matthiessen, F. O ..... 10 Wall St., N. Y. City.  
 1899 Meader, A. Lloyd ..... Harris Ave., Norwood, Cincinnati, O.  
 1900 Medcalf, George T ..... Box 280, Eureka, Humboldt Co., Cal.  
 1898 Mehrbach, William ..... 56 E. 72d St., N. Y. City.  
 1877 Merz, Henry ..... 55 Maiden Lane, N. Y. City.  
 1900 Mihalovitch, Sidney F ..... 829 Hutchins Ave., Avondale, Cincinnati, O.  
 1890 OAKES, F. J ..... 58 Stone St., N. Y. City.  
 1900 Olshausen, Bruno .. ..... Box 127, Stanford University, Cal.  
 1898 PFEIFFER, Clarendon H .. 1 W. 81st St., N. Y. City.  
 1898 Pope, W. C ..... 220 Devonshire St., Boston, Mass.  
 1899 Porter, John J ..... Observatory Ave., Hyde Park, Cincinnati, O.  
 1899 Powell, Thomas H ..... 53 S. Main St., South Norwalk, Conn.  
 1899 Pray, D. M ..... 508 Broadway, So. Boston, Mass.  
 1878 PRENTICE, W. P ..... 52 Broadway, N. Y. City.  
 1900 Pretzfeld, Charles J ..... 1211 Madison Ave., N. Y. City.  
 1900 REESE, Herbert J ..... Bozeman, Mont.  
 1877 Renwick, E. S ..... 19 Park Place, N. Y. City.  
 1895 Reubens, Charles M ..... 108 W. 113th St., N. Y. City.  
 1898 Rickards, Burt R ..... 162 Salem St., Malden, Mass.  
 1899 Robeson, Anthony M ..... 371 W. 120th St., N. Y. City.  
 1899 Roller, H. C ..... Dick, Ridout & Co., Cobourg, Ontario.  
 1898 Ruhl, Louis ..... Box 1999, N. Y. City.  
 1899 Russell, George F ..... Russell Paper Co., Lawrence, Mass.  
 1894 SCHEEL, Wm. H ..... 78 Pine St., N. Y. City.  
 1876 SENFF, CHARLES H ..... Whitestone, Queens Co., N. Y.  
 1900 Shilstone, Herbert M ..... 166 St. James Pl., Brooklyn, N. Y.  
 1898 Smith, Burnett ..... 144 W. 73d St., N. Y. City.  
 1900 Spragg, Frank A ..... Bozeman, Mont.  
 1898 Stadermann, Albert L ..... 533 Betts St., Cincinnati, O.  
 1897 Steenken, J. G ..... Box 2005, N. Y. City.  
 1900 Stierlin, E ..... 1110 Queen City Ave., Cincinnati, O.  
 1900 Stifel, Walter H ..... 1319 Locust St., Allegheny, Pa.  
 1890 Stiff, George ..... 439 Ditmar Ave., Borough of Queens, N. Y. City.  
 1877 Stursberg, J. A ..... W. Stursberg, Schell & Co., 79-81 Leonard St., N. Y. City.  
 1899 Summey, Albert E ..... Box 36, South Amboy, N. J.  
 1899 TEASDALE, Wm. S ..... 625-7 Walnut St., Cincinnati, O.  
 1894 Terheun, Peter O ..... Hohokus, Bergen Co., N. J.  
 1898 Thompson, J. Howard ..... 372 Atlantic Ave., Boston, Mass.  
 1899 Treiber, C ..... 372 Atlantic Ave., Boston, Mass.

1895	Tuckerman, Alfred	342 W. 57th St., N. Y. City.
1898	Tufts, John L.	433 Penn St., Camden, N. J.
1898	Turnbull, Arthur	38 Kilby St., Boston, Mass.
1897	Turnquist, C. M	2458 Wentworth Ave., Chicago, Ill.
1896	Twining, F. E	Lock Box 693, Fresno, Cal.
1895	WALDMAN, Louis I	P. O. Box 162, Albany, N. Y.
1900	Warren, Robert C.	919 S. 6th St., Terre Haute, Ind.
1900	Waters, Oliver G.	223 5th Ave., Pittsburg, Pa.
1900	Watson, Henry E. G	117 Martien Hall, Easton, Pa.
1900	Webb, Ernest H	1256 Massachusetts Ave., Cambridge, Mass.
1900	Willard, H. H	Union City, Mich.
	Total	123

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Members	1546
Associates	123
Honorary	10
Total	1679

# GEOGRAPHICAL LIST.

FOR FULL ADDRESSES SEE ALPHABETICAL LIST OF MEMBERS.

## ALABAMA.

### AUBURN.

Hare, C. L.  
Ross, B. B.

### BIRMINGHAM.

Burn, Harry  
Hancock, David  
Harris, J. R.  
Kelly, F. G.  
Linton, J. H.  
Norman, G. M.

### EUSLEY.

Belden, A. W.

### GADSDEN.

Walker, P. H.

### TALLADEGA.

Miller, F. W.

### UNIVERSITY.

Persons, A. A.

### WOODWARD.

Evans, Ernest.

## ARIZONA.

### BISBEE.

Closson, C. D.  
Nichols, H. T.

### CLIFTON.

Smith, J. D. A.

### CRITTENDEN.

Neilson, Thomas

### JEROME.

Mather, H. A.

### TUCSON.

Guild, F. N.

## ARKANSAS.

### FAYETTEVILLE.

Menke, A. E.  
Teller, G. L.

## CALIFORNIA.

### BERKELEY.

Blasdale, W. C.  
O'Neill, Edmund  
Rising, W. B.

### EUREKA.

Medcalf, G. T. (A)\*

### FRESNO.

Twining, F. E. (A)

### LOS ANGELES.

Bullard, F. D.  
Fosdick, E. H.  
Hildreth, E. T. (A)  
Labonde, Leon  
Schoonmaker, H.  
Wade, E. M.

### OAKLAND.

Miller, H. E.  
Ross, H. W.

### ONTARIO.

Gooch, G. W.

### PALO ALTO.

Emery, A. L.  
Loeser, R. M. (A)

### PASADENA.

Barlow, W. H.  
Behr, Arno  
Croftan, A. C.  
Gaylord, W. K.

### PINOLE.

Quinan, K. B.  
Smith, F. W.

\* (A) = Associate.

CALIFORNIA (*continued*).

## SAN FRANCISCO.

Best, Otto  
 Burr, E. C.  
 Curtis, Marvin  
 DeConinck, Frank  
 Falkenau, Louis  
 Green, F. T.  
 Hanks, A. A.  
 Martin, M. A.  
 Michaelis, Theodore  
 Peyton, W. C.  
 Wrampelmeier, T. J.  
 Wulf, H. C.

## SANTA ANA.

Dunn, W. A.

## SANTA MARIA.

Atkinson, J. W.  
 Norris, R. S.

## SELBY.

James, G. A.

## STANFORD UNIVERSITY.

Lenox, L. R.  
 Olshausen, Bruno (A)  
 Richardson, G. M.  
 Stillman, J. M.  
 Young, S. W.

## VALLEJO.

Rippetoe, J. J.

## COLORADO.

## BOULDER.

Palmer, C. S.

## COLORADO SPRINGS.

Evans, W. L.

## DENVER.

Field, Chas., 3rd  
 Low, A. H.  
 Parmelee, H. C.  
 Pearce, Richard

## LEADVILLE.

Elliott, E. C.  
 Gallaher, P. C.

## OURAY.

Carr, L. B.

## UNIVERSITY PARK.

Engle, W. D.

## CONNECTICUT.

## BRIDGEPORT.

Graves, G. H.

## GLASTONBURY.

Hurlburt, E. B.

## GREENWICH.

Wakeman, A. J.

## HARTFORD.

Riggs, R. B.  
 Souther, Henry

## MIDDLETOWN.

Atwater, W. O.  
 Bradley, W. P.

## NEW HAVEN.

Barnes, Bayard  
 Boltwood, B. B.  
 Browning, P. E.  
 Campbell, G. F.  
 Chittenden, R. H.  
 Gooch, F. A.  
 Johnson, S. W.

NEW HAVEN (*continued*).

McFarland, B. W.  
 Mixter, W. G.  
 Osborne, T. B.  
 Phelps, I. K.  
 Smith, H. E.  
 Wells, H. L.  
 Wheeler, H. L.  
 Winton, A. L.

## SOUTH MANCHESTER.

Cheney, J. P.

## SOUTH NORWALK.

Powell, T. H. (A)

## STAMFORD.

Getman, F. H.  
 Williams, J. T.

## WALLINGFORD.

Cottle, G. T.

## WESTVILLE.

Johnson, T. B.



## DELAWARE.

## NEWARK.

Wolf, T. R.

## WILMINGTON.

du Pont, A. I. (A)  
 du Pont, F. G.  
 Krebs, H. J.

## DISTRICT OF COLUMBIA.

## BROOKLAND.

Holton, F. A.

## GEORGETOWN.

Deck, J. J.

## WASHINGTON.

Allen, E. W.  
 Beal, W. H.  
 Benjamin, Marcus  
 Bigelow, W. D.  
 Bolton, H. C.  
 Byrnes, E. A.  
 Cameron, F. K.  
 Chatard, T. M.  
 Chesnut, V. K.  
 Clarke, F. W.  
 Clarke, Thomas  
 Crampton, C. A.  
 Cutter, W. P.  
 Day, D. T.  
 de Schweinitz, E. A.  
 Dewey, F. P.  
 Dorset, F. M.  
 Dow, A. W.  
 Doyle, A. M.  
 Ely, C. R.  
 Ely, G. S.  
 Ewell, E. E.  
 Fireman, Peter  
 Fischer, L. A.  
 Georgii, Max  
 Griffin, J. H.  
 Griffin, J. J.  
 Griffith, S. H.  
 Hargrove, J. O.  
 Haywood, J. K.  
 Hill, E. A.  
 Hillebrand, W. F.  
 Hopkins, N. M.

WASHINGTON (*continued*).

Jessup, A. E.  
 Kelly, D. J.  
 Krug, W. H.  
 Langworthy, C. F.  
 Littlewood, J. B.  
 Loew, Oscar  
 Mew, W. M.  
 Miller, S. C.  
 Mills, J. S.  
 Munroe, C. E.  
 Munson, L. S.  
 Newton, E. S.  
 Parker, C. L.  
 Patrick, G. E.  
 Portner, E. G.  
 Runyan, E. G.  
 Seaman, W. H.  
 Simons, F. D.  
 Spencer, G. L.  
 Steiger, George  
 Stetson, F. O.  
 Stokes, H. N.  
 Suter, Frank  
 Tassin, Wirt  
 Townsend, C. P.  
 Trescot, T. C.  
 Tucker, G. P.  
 Van Dyck, E. M.  
 Warder, R. B.  
 Westessan, J. P. L.  
 White, C. H.  
 Whitehead, Cabell  
 Wiley, H. W.  
 Witherspoon, T. A.  
 Wolff, F. A., Jr.  
 Workman, H. C.  
 Yount, C. E.

## FLORIDA.

## JACKSONVILLE.

Sedding, G. H. P.

## LAKE CITY.

Blair, A. W.  
 Miller, H. K.

## GEORGIA.

## ATHENS.

Herty, C. H.  
White, H. C.

## ATLANTA.

Emerson, W. H.  
Mallory, J. H.  
McCandless, J. M.  
Payne, G. F.  
Yeates, W. S.

## AUGUSTA.

Pitman, John

## MOSCOW.

Avery, Samuel  
Miller, A. S.

## AURORA.

Baxter, W. T.  
Thurnauer, Gustav  
Wickhorst, M. H.

## BERWYN.

Willey, O. G.

## BLOOMINGTON.

Graham, R. O.

## CHAMPAIGN.

Bevier, Isabel  
Hopkins, C. G.  
Koch, F. C.  
Palmer, A. W.

## CHICAGO.

Adams, Maxwell  
Ashby, Geo. J. M. (A)  
Bach, August  
Bernhard, Adolph  
Brown, W. B.  
Carnell, W. C.  
Carr, R. F.  
Cayvan, L. L.  
Chamberlain, G. E.  
Chapman, D. W.  
Clement, Arthur A.  
Cluff, C. B.  
Converse, W. A.  
Dains, F. B.  
Davidson, G. M.  
Drake, C. F.  
Ellis, G. H.  
Flynn, O. R.  
Ford, A. P.  
Germer, J. W. (A)  
Grabfield, J. P.

## MILLEDGEVILLE.

Beeson, J. L.

## ROME.

Graham, S. L.

## SAVANNAH.

Tennille, G. F.  
Wesson, David

## IDAHO.

## ILLINOIS.

CHICAGO (*continued*).

Gudeman, Edward  
Haines, W. S.  
Hoskins, Wm.  
James, G. W.  
Kiehn, J. F. (A)  
Laudig, O. O.  
Lengfeld, Felix  
Linebarger, C. E.  
Lloyd, George  
Long, J. H.  
Mackenzie, J. K.  
Maharg, W. S.  
Manns, A. G.  
Mason, F. P.  
McClement, W. T.  
McKenzie, R. M.  
Moore, B. L.  
Nelson, E. K.  
Nelson, N.  
Patterson, C. W.  
Puckner, W. A.  
Root, W. W.  
Rudnick, P. F. A.  
Sarles, E. H.  
Schoch, E. P.  
Smith, W. R.  
Summers, B. S.  
Swenson, M.  
Thorburn, A. D.  
Turnquist, C. M. (A)  
Vreeland, C. D.  
Wagner, T. B.  
Waterman, C. N.  
Williams, L. S.

ILLINOIS (*continued*).

## DEER PARK GLEN.

Passolt, H. A.

## ENGLEWOOD.

Smith, A. L.

## EVANSTON.

Young, A. V. E.

## GALESBURG.

Griffith, H. E.

## KEWANEE.

Sandford, W. E.

## MONMOUTH.

Swan, J. N.

## OAK PARK.

Smyth, G. A.

## PEKIN.

Terne, Bruno

Wolfe, J. V., Jr.

## PEORIA.

Breyer, Theodor

Teeter, C. W.

Wilson, H. T.

## PERU.

Lihme, C. B.

## ROCKFORD.

Mommers, Richard

Sovereign, C. L.

## URBANA.

Grindley, H. S.

Parr, S. W.

## WAUKEGAN.

Hibbard, P. L.

## WEST PULLMAN.

Woods, R. M.

## INDIANA.

## AETNA.

Hall, Clarence

Harrington, E. M.

## BLOOMINGTON.

Lyons, R. E.

## GREENCASTLE.

Baker, P. S.

## INDIANAPOLIS.

Benton, G. W.

Doan, Martha

Hurty, J. N.

## LAFAYETTE.

Conner, S. D.

Huston, H. A.

Jones, W. J., Jr.

Stone, W. E.

## MUNCIE.

Dickson, J. C.

## TERRE HAUTE.

Noyes, W. A.

Warren, R. C. (A)

## IOWA.

## AMES.

Bennett, A. A.

Weems, J. B.

## CEDAR RAPIDS.

Barrett, J. M.

## DES MOINES.

Davis, Floyd

Macy, S. R.

## IOWA CITY.

Andrews, L. W.

## SIOUX CITY.

Becher, J. B.

Duryea, C. B.

## STUART.

Treat, J. A.

## KANSAS.

## ARGENTINE.

Colley, B. T.

Hatchett, R. H.

Hofmann, Ottokar

Koelle, Carl

Lippincott, W. B.

## ATCHISON.

Knerr, E. B.

## BALDWIN.

Bauer, Wm. C.

KANSAS (*continued*).

## LAWRENCE.

Bailey, E. H. S.  
Bartow, Edward  
Blake, L. I.  
Franklin, E. C.

## MANHATTAN.

Willard, J. T.

## OTTAWA.

Yates, J. A.

## KENTUCKY.

## FORT THOMAS.

Keiser, Marshall (A)

## LEXINGTON.

Kastle, J. H.  
Peter, A. M.  
Scovell, M. A.

## LOUISVILLE.

Burk, W. E.  
Palmer, Chase

## MIDDLESBOROUGH.

Sanderson, John

## NEWPORT.

Hayes-Campbell, J.

## LOUISIANA.

## BATON ROUGE.

Coates, C. E., Jr.

## CALHOUN.

Bird, Maurice

## JACKSON.

Sullivan, J. M.

## KEACHIE.

Thigpen, J. H.

## LULING P. O.

Becnel, L. A.

## NEW ORLEANS.

Blouin, R. E.  
Eustis, A. C.  
Goodrich, A. L.  
Johnson, F. C.  
Taylor, H. W.

## PATTERSON.

Edson, Hubert

## MAINE.

## BANGOR.

Hamlin, Addison

## BATH.

Sawyer, H. B.

## CUMBERLAND MILLS.

Gabriel, G. A.

## GREAT WORKS.

Larchar, A. B.  
Wentworth, W. V.

## ORONO.

Aubert, A. B.  
Rogers, Allen

## PORTLAND.

Yeaton, A. C.

## SOUTH GARDINER.

Martin, Henry

## WEST PARIS.

Moore, H. K.

## MARYLAND.

## BALTIMORE.

Abel, J. J.  
Blackshear, C. C.  
Browne, A. L.  
Case, W. A.  
Dohme, A. R. L.  
Gascoyne, W. J.  
Glaser, Chas.

BALTIMORE (*continued*).

Glenn, Wm.  
Hershey, A. N.  
Hillyer, W. E.  
Hoffmann, P. C.  
Johns, John  
Keller, Edward  
Lehmann, G. W.

MARYLAND (*continued*).BALTIMORE (*continued*).

Penniman, W. B. D.  
Remsen, Ira  
Simmons, W. W.  
Simon, Wm.  
Van Gundy, C. P.

## BERWYN.

Chace, E. M.

## COLLEGE PARK.

McDonnell, H. B.  
Patterson, H. J.  
Skinner, Wm. W.  
Veitch, F. P.

## INDIAN HEAD.

Kniffen, Frederick

## MT. WASHINGTON.

Whitehead, R. L.

## SPARROWS POINT.

Lyons, P. D.  
Randall, N. M.

## MASSACHUSETTS.

## ADAMS.

Busby, F. E.

## AMHERST.

Goessmann, C. A.  
Haskins, H. D.  
Hopkins, A. J.  
Lindsey, J. B.  
Wellington, Charles

## ANDOVER.

Hill, H. H.  
Ripley, P. F.

## ARLINGTON.

Frost, H. V.

## AUBURNDALE.

Norton, A. P.

## BOSTON.

Atteaux, F. E. (A)  
Atwood, F. W.  
Babb, E. E.  
Baird, J. W.  
Bardwell, F. L.  
Bennett, F. W.  
Billings, E. F.  
Blanchard, A. A.  
Carmichael, Henry  
Chapin, L. P.  
Clapp, E. H. (A)  
Clark, H. W.  
Coburn, D. L.  
Cochrane, Hugh (A)  
Cowen, G. A.  
Crafts, J. M.  
Davenport, B. F.  
Durfee, W. C.  
Durkee, W. C.  
Eyster, G. S.

BOSTON (*continued*).

Fay, Henry  
Forbes, F. B.  
Gagnebin, C. L. (A)  
Gill, A. H.  
Glaesel, Theodore  
Green, E. H.  
Hall, A. W. (A)  
Hall, W. T.  
Herrick, R. F.  
Hills, W. B.  
Holmes, V. F. (A)  
Hopkins, Erastus  
Horsford, R. F.  
Howard, A. P. (A)  
Howe, C. A. (A)  
Howe, E. P.  
James, L. S.  
Jenkins, C. D.  
Knight, G. W. (A)  
Lanzendoerfer, George  
Leach, A. E.  
Little, A. D.  
Lockwood, R. G.  
Lythgoe, H. C.  
Means, R. F.  
Miles, G. W., Jr.  
Moore, F. J.  
Mulliken, S. P.  
Norris, J. F.  
Noyes, A. A.  
Nye, W. B.  
Phelan, J. W.  
Pickert, L. W.  
Pope, T. E.  
Pope, W. C. (A)  
Pratt, G. H.  
Prescott, S. C.  
Redpath, L. W.

MASSACHUSETTS (*continued*).BOSTON (*continued*).

Richards, E. H.  
 Richards, R. H.  
 Rosentwist, B. G. A.  
 Russell, L. K.  
 Scudder, Heyward  
 Seidensticker, L. J.  
 Sharples, P. P.  
 Sharples, S. P.  
 Sherman, G. W.  
 Smith, J. W.  
 Talbot, H. P.  
 Thompson, J. H. (A)  
 Thorp, F. H.  
 Thorpe, E. E.  
 Treiber, C. (A)  
 Turnbull, Arthur (A)  
 Walker, W. H.  
 Wason, R. S.  
 Weston, R. S.  
 Whitney, W. R.  
 Wilder, S. W., Jr.  
 Williams, H. J.  
 Williams, R. P.  
 Wood, E. S.  
 Woodman, A. G.

## BRIGHTON.

Hapgood, C. W.

## BROOKLINE.

Howard, Henry  
 Lee, J. C.  
 Swan, C. M.

## CAMBRIDGE.

Behr, G. E., Jr.  
 Black, O. F.  
 Bonnet, Frederic, Jr.  
 Coggeshall, G. W.  
 Comey, A. M.  
 Earle, R. B.  
 Hill, H. B.  
 Jackson, C. L.  
 Mellen, E. D.  
 Merigold, B. S.  
 Parker, H. N.  
 Phinney, J. I.  
 Richards, T. W.  
 Rolfe, G. W.  
 Sanger, C. R.  
 Webb, E. H. (A)  
 Williams, S. E.

## CAMBRIDGEPORT.

Baldwin, C. E.  
 Loveland, J. W.  
 Price, R. B.

## CANTON.

Lustig, A. L.

## CHARLESTOWN.

Farwell, S. A.

## CHELSEA.

Butler, W. F. (A)

## EAST BOSTON.

Le Bosquet, Maurice

## EAST BRIDGEWATER.

Smith, H. T.

## EVERETT.

Cochrane, A. L.

Olsson, Gustaf

Stantial, F. G.

## FELLS.

Piper, W. E.

## FITCHBURG.

Holman, G. M.

## GREENDALE.

Sweetser, R. C.

## HOLYOKE.

Downey, J. E.

## HYDE PARK.

Perkins, A. S.

## LAWRENCE.

Alden, John

Beach, I. E.

Collins, J. A., Jr.

Gage, S. DeM.

Greenwood, H. D.

Livermore, W. D.

Moran, G. A.

Russell, G. F. (A)

## LITTLETON.

Clafin, A. A.

Weld, F. C.

## LOWELL.

Ames, G. E. (A)

Atwood, W. P.

Butler, Paul (A)

Coburn, A. S.

Hobbs, A. F. (A)

Irish, C. W.

Jenkins, E. D.

Newell, L. C.

Olney, L. A.

Spencer, G. C.

## LYNN.

Darke, J. M. (A)

Tucker, C. W.

MASSACHUSETTS (*continued*).

## MALDEN.

Hill, W. G., Jr.  
Rickards, B. R. (A)  
Wakefield, F. P.

## MELROSE.

Holden, E. F.

## MELROSE HIGHLANDS.

Pickering, O. W.

## NEW BEDFORD.

Allen, C. R.  
Allen, W. S.  
Ashley, H. E.

## NEWBURYPORT.

Coffin, E. F. (A)  
Thompson, M. S.

## NEWTON HIGHLANDS.

Hollis, F. S.

## NORTH ADAMS.

Lichtenstein, A. F.

## NORTHAMPTON.

Stoddard, J. T.

## NORTH ANDOVER.

Bannan, J. F.

## NORTH CAMBRIDGE.

Adams, Isaac  
Adams, W. O.

## NORTH WEYMOUTH.

Bates, H. R.  
Benson, D. H.

## NORTH WOBURN.

Walls, A. W.

## PEABODY.

Underwood, G. R.

## ROSLINDALE.

Watkins, W. H.

## ROXBURY.

Mork, H. S.  
Rosenberg, M. A.  
White, L. B.

## SALEM.

Goodhue, L. H.

## SOMERVILLE.

Kendall, A. I. (A)

## SOUTH BOSTON.

Bassett, G. O.  
Pray, D. M. (A)  
Sawyer, H. E.

## SOUTH BRAINTREE.

Pitkin, C. A.

## STONEHAM.

Patch, E. L.

## SWAMPSCOTT.

Thomson, Elihu

## WALTHAM.

Smith, A. C.

## WATERTOWN.

Priest, G. W.  
Weston, D. B.

## WELLESLEY.

Bragg, C. A.  
Jackson, Florence  
Roberts, C. F.

## WILLIAMSTOWN.

Mears, Leverett

## WOBURN.

Dickerman, J. C.

## WOLLASTON.

Kenney, C. B.

## WORCESTER.

Buffington, E. L.  
Desper, E. W.  
Dunlap, F. L.  
Eddy, H. P.  
Given, Arthur  
Jennings, W. L.  
Kinnicutt, L. P.  
Marble, J. R. (A)  
Moore, G. D.  
O'Regan, D. F.  
Perry, J. H.  
Small, F. H.  
Smith, E. L.  
Snyder, W. H.  
Trotz, J. O. E.

## MICHIGAN.

## AGRICULTURAL COLLEGE.

Kedzie, R. C.

## ALMA.

Jessurun, David

## ANN ARBOR.

Allen, L. E. (A)  
Bigelow, S. L.  
Campbell, E. D.

MICHIGAN (*continued*).ANN ARBOR (*continued*).

Freer, P. C.  
Gomberg, M.  
Hulett, G. A.  
Johnson, O. C.  
Prescott, A. B.  
Stevens, A. B.  
Sullivan, E. C.  
Trowbridge, P. F.  
White, A. H.

## CARO.

Davoll, D. L.

## COLDWATER.

Brown, H. E.  
Gerlach, Oscar  
Post, F. I.

## DEARBORN.

Duffield, S. P.

## DETROIT.

Carman, J. S.  
Diehl, O. C.  
Edgar, C. G.  
Foster, A. D. (A)  
Francis, J. M.  
Frazee, F. H.  
Knapp, R. E.  
Knox, J. W. T.  
Leach, M. F.  
Shattuck, A. F.  
Sherrard, C. C.

## HASTINGS.

Kunze, W. F.

## HIBBING.

Lerch, Fred.

## LITCHFIELD.

Anderson, C. A. (A)

## MINNEAPOLIS.

Appleby, W. R.  
Carel, H. C.  
Drew, C. W.  
Frankforter, G. B.  
Glasoe, P. M.  
Meeds, A. D.  
Nicholson, E. E.

DETROIT (*continued*).

Sundstrom, Carl  
Tibbals, W. I.  
Ware, E. J.

## IRON MOUNTAIN.

Brewster, E. E.  
Hardenburgh, L. M.

## KALAMAZOO.

Hartman, W. E.  
Jenks, S. G.  
Todd, A. M.

## LANSING.

Doolittle, R. E.  
Hess, W. H.  
Kedzie, F. S.

## MIDLAND.

Dow, H. H.

## SOUTH LAKE LINDEN.

Heath, G. L.

## TRENTON.

Button, Ok  
Sundstrom, K. J.

## UNION CITY.

Lundteigen, Andreas  
Willard, H. H. (A)

## YPSILANTI.

Peet, B. W.

## MINNESOTA.

MINNEAPOLIS (*continued*).

Roberts, W. H.  
Sidener, C. F.  
Van Cleve, C. E.  
Wulling, F. J.

## MOUNT IRON.

Maury, G. P.

## NORTHFIELD.

Metcalf, W. V.

## ST. ANTHONY PARK.

Snyder, Harry

## ST. PAUL.

Hummel, J. A.  
Julian, Frank

## MISSISSIPPI.

## AGRICULTURAL COLLEGE.

Hand, W. F.

## CLINTON.

Provine, J. W.

## UNIVERSITY.

Jones, R. W.

## WATER VALLEY.

Parks, R. M.



## MISSOURI.

## ASHBURN.

Riederer, E. J.

## COLUMBIA.

Brown, W. G.

Cady, W. B.

Calvert, Sidney

## JOPLIN.

Cleveland, W. P.

Mixer, C. T.

## KANSAS CITY.

Irwin, E. P.

Miller, A. R.

Moechel, J. R.

KANSAS CITY (*continued*).

Nathan, A. F., Jr.

Nishkian, P. F.

Van Brunt, Charles

## ST. LOUIS.

Arnold, F. N., Jr.

Chauvenet, W. M.

Frerichs, F. W.

Getz, W. H.

Hunicke, H. A.

Keiser, E. H.

Mallinckrodt, Edward (A)

Nickel, H. L.

Whittier, C. T.

## MONTANA.

## ANACONDA.

Bellam, H. L.

Cairns, F. I.

Hoff, Karl

Smith, E. A.

Terry, J. P.

Wilkinson, T. K.

## BELT.

Thomas, W. S.

## BOZEMAN.

Burke, Edmund (A)

Cobleigh, W. M.

Cockrill, Irvin

Reese, H. J. (A)

Shaw, W. T.

Spragg, F. A. (A)

Traphagen, F. W.

## BUTTE.

Clark, Clara (A)

Smolt, F. O.

## GILT EDGE.

Shaw, H. I.

## GOULD.

Harsh, S. A.

## HELENA.

Starz, Emil

## MARYSVILLE.

Sharwood, W. J.

## VIRGINIA CITY.

Caldwell, T. O.

## NEBRASKA.

## CRETE.

Banghart, E. D.

## LINCOLN.

Beans, H. T.

Bouton, Rosa

Fossler, M. L.

Gere, M. C.

Hiltner, M. E.

Hiltner, R. S.

Lyon, T. L.

Nicholson, H. H.

Nikaido, Y.

LINCOLN (*continued*).

Thatcher, R. W.

White, John

## OMAHA.

Jones, L. J. W.

Robinson, W. S.

## UNIVERSITY PLACE.

Alway, F. J.

## WAVERLY.

Riddell, D. F.

## NEVADA.

## VIRGINIA CITY.

Fielding, F. E.

## ST. LOUIS.

Schoen, Joseph

## NEW HAMPSHIRE.

<p style="text-align: center;"><b>CONCORD.</b></p> <p>Coit, J. M. Sears, F. E.</p> <p style="text-align: center;"><b>DOVER.</b></p> <p>Duckworth, H. S.</p> <p style="text-align: center;"><b>DURHAM.</b></p> <p>Lazell, E. W. Morse, F. W. Parsons, C. L.</p> <p style="text-align: center;"><b>EXETER.</b></p> <p>White, G. R.</p>	<p style="text-align: center;"><b>HANOVER.</b></p> <p>Bartlett, E. J.</p> <p style="text-align: center;"><b>KERNE.</b></p> <p>Ellis, Carleton (A)</p> <p style="text-align: center;"><b>MANCHESTER.</b></p> <p>Robbins, W. K. Schaeffer, Henri</p> <p style="text-align: center;"><b>PORTSMOUTH.</b></p> <p>Moat, C. P.</p>
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## NEW JERSEY.

<p style="text-align: center;"><b>AMPERE.</b></p> <p>Jacobs, C. B.</p> <p style="text-align: center;"><b>BAYONNE.</b></p> <p>Wadman, W. E.</p> <p style="text-align: center;"><b>BELLEVILLE.</b></p> <p>Fleck, Herman Simon, S. E.</p> <p style="text-align: center;"><b>BLOOMFIELD.</b></p> <p>Cornelison, R. W.</p> <p style="text-align: center;"><b>CAMDEN.</b></p> <p>Boyer, C. S. Skinner, H. J. Tufts, J. L. (A)</p> <p style="text-align: center;"><b>DOVER.</b></p> <p>Penniman, R. S.</p> <p style="text-align: center;"><b>EAST ORANGE.</b></p> <p>Aylsworth, J. W. Williams, S. W.</p> <p style="text-align: center;"><b>EDGEWATER.</b></p> <p>Motion, John</p> <p style="text-align: center;"><b>ELIZABETH.</b></p> <p>Bailey, R. W. Gustin, G. H. Luster, H. A. Smith, F. J. Smoot, A. M. Thomson, M. J.</p> <p style="text-align: center;"><b>ENGLEWOOD.</b></p> <p>Grosvenor, W. M., Jr.</p> <p style="text-align: center;"><b>GLOUCESTER CITY.</b></p> <p>Miner, H. S.</p> <p style="text-align: center;"><b>HACKENSACK.</b></p> <p>Krause, O. H.</p> <p style="text-align: center;"><b>HIGH BRIDGE.</b></p> <p>Le Boutillier, Clement</p>	<p style="text-align: center;"><b>HOBOKEN.</b></p> <p>Geyer, W. E. Leeds, A. R. Morton, Henry Sieker, F. A. Stillman, T. B.</p> <p style="text-align: center;"><b>HOBOKUS.</b></p> <p>Annison, F. G. (A) May, G. H. Terheun, P. O. (A) Wynkoop, Gillett</p> <p style="text-align: center;"><b>JERSEY CITY.</b></p> <p>Burleigh, W. F. Hale, F. M. Herrick, W. H. McKelvey, J. W. Niese, H. E. Stearns, T. C. Sticht, G. A. H. Taylor, D. W. Tompkins, Vreeland</p> <p style="text-align: center;"><b>LAKEWOOD.</b></p> <p>Harris, E. P.</p> <p style="text-align: center;"><b>MAURER.</b></p> <p>Aller, F. D.</p> <p style="text-align: center;"><b>MILLVILLE.</b></p> <p>Barton, G. E.</p> <p style="text-align: center;"><b>MONTCLAIR.</b></p> <p>Crane, Fred.</p> <p style="text-align: center;"><b>NEWARK.</b></p> <p>Baldwin, H. B. Bassett, W. H. Cawley, John Colby, E. A. Gibson, H. W. Hewson, J. H. Pomeroy, C. T.</p>
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NEW JERSEY (*continued*).NEWARK (*continued*).

Reese, C. L.  
 Seher, August  
 Starr, H. F.  
 Thurlow, Nathaniel  
 Van Ingen, D. A.  
 Wiener, William

## NEW BRUNSWICK.

Cathcart, C. S.  
 Chester, A. H.  
 Cook, R. A.  
 Morgan, J. L. R.  
 Myers, W. S.  
 Speyers, C. L.  
 Street, J. P.  
 Voorhees, E. B.  
 Voorhees, L. A.

## NEW DURHAM.

Fuelling, J. L.

## OAKLAND.

Borland, C. R.  
 Hawkins, Henry  
 Willcox, F. A.

## ORANGE.

Parker, C. E.  
 Vanderpoel, Frank

## PASSAIC.

Hall, E. J.  
 Lee, Waldemar

## PATERSON.

Granja, Rafael  
 Haigh, Frederic  
 Hunziker, Aug.  
 Reinus, Bernhard

## PEMBERTON.

Saltar, J. C.

## PERTH AMBOY.

Fadé, Louis  
 Knorr, A. E.

## POMPTON LAKES.

Baker, Theodore  
 Pitman, J. R.

## PRINCETON.

McCay, L. W.  
 Neher, F.

## RIDGEWOOD.

Briggs, T. L.

## ROSELLE.

Jouët, C. H.

## RUSTIC.

Van Gelder, A. P.

## RUTHERFORD.

Van Riper, G. B.

## SHORT HILLS.

Axtell, F. C.

## SOMERVILLE.

Wigfall, E. N.

## SOUTH AMBOY.

Burnside, C. F.  
 Summey, A. E. (A)

## SUMMIT.

Riggs, G. W.  
 Merriam, H. F.

## TRENTON.

Mumper, W. N.

## WOODBINE.

Lipman, J. G.

## NEW MEXICO.

## SOCORRO.

Phalen, W. C.

## NEW YORK.

## ALBANY.

Dederick, P. K., Jr. (A)  
 Michaelis, Gustavus  
 Tucker, W. G.  
 Waldman, L. I. (A)  
 Wheeler, E. J.

## BINGHAMTON.

Dustin, G. K.

## BROOKLYN.

Allen, C. M.  
 Baker, H. M.  
 Bartley, E. H.  
 Beck, O. C.  
 Bird, H. S.  
 Booraem, J. V. V.  
 Bruckmann, G. T.  
 Bunker, H. A. (A)

NEW YORK (*continued*).BROOKLYN (*continued*).

Casamajor, Walter  
 Commiskey, A. F.  
 Condit, L. C. (A)  
 Cook, C. G.  
 Cutts, H. E.  
 Davidson, G. H. (A)  
 Deghuée, J. A.  
 Doerflinger, W. F.  
 Eccles, D. C. (A)  
 Eccles, R. G.  
 Enequist, John  
 Fay, I. W.  
 Fitz-Randolph, R. B.  
 Gallivan, F. B.  
 Goldschmidt, S. A.  
 Goodenough, R. J. (A)  
 Hale, A. C.  
 Hancock, W. J.  
 Haslwanter, Charles (A)  
 Heidenhain, H.  
 Hero, Ann  
 Herreshoff, J. B. F.  
 Hodgson, E. H.  
 Hyde, F. S.  
 Jackson, D. D.  
 Keator, C. E.  
 Kendall, E. D.  
 Kent, W. H.  
 King, F. T.  
 Lawler, C. J.  
 Levison, W. G.  
 Mangan, D. C.  
 Mathews, J. A.  
 Maywald, F. J.  
 McGeorge, Arthur  
 Miller, P. S.  
 Millwood, J. P.  
 Parsons, C. C.  
 Peckham, S. F.  
 Pierson, W. C.  
 Perkins, T. S.  
 Schaak, M. F.  
 Schedler, R. W.  
 Schiller, L. J.  
 Seldner, Rudolph  
 Share, W. W.  
 Shilstone, H. M. (A)  
 Squibb, E. R.  
 Stocker, J. H.  
 Van Slooten, Wm.  
 Volckening, G. J.  
 von Egloffstein, C.  
 Walker, H. V.  
 Weed, H. T.  
 Whipple, G. C.

## BUFFALO.

Carpenter, T. B.  
 Denham, H. H.  
 Herger, C. G.  
 Hill, H. M.  
 Miller, J. A.  
 Sy, A. P.  
 Wing, H. H.

## CENTER MORICHES.

Masury, J. W. (A)

## CLINTON.

Higbee, H. H.

## COLLEGE POINT.

Edgerly, D. W.

## FAR ROCKAWAY.

Ackerman, F. W.

## FLUSHING.

Clark, Edmund  
 Ferguson, W. C.  
 Goodridge, E. A. (A.)  
 Ward, D. W.

## GARDEN CITY.

Ekeley, J. B.  
 Hewitt, E. R.

## GENEVA.

Cook, A. D.  
 Fuller, F. D.  
 Hart, E. B.  
 Le Clerc, J. A.  
 Mudge, C. W.  
 Van Slyke, L. L.

## GLENS FALLS.

De Roode, Rudolf  
 Dixon, J. B.  
 Kendall, R. E.

## GREEN ISLAND.

Wachter, L. M.

## HAMBURG.

Divine, R. E.

## HAMILTON.

McGregory, J. F.

## HART PARK.

Allen, R. F.

## HASTINGS-ON-HUDSON.

Gotthelf, A. H.  
 Zinsser, F. G.

## HULETT'S LANDING.

Peters, Andrew

## NEW YORK CITY (continued).

Baer, S. H.  
 Berry, W. G.  
 Bertelli, R.  
 Choff, Ernst  
 +, M. T.  
 . K.  
 Samuel  
 Leopold  
 (A)

JS

d.

ery, J. L.  
 rson, E. N.  
 remus, C. A.  
 Joscher, Henry  
 Drummond, I. W.  
 Dunham, E. K.  
 Du Vivier, E. H.  
 Eimer, August  
 Elliott, A. H.  
 Ellsworth, Wm. (A)  
 Emmens, S. H.  
 Endemann, Hermann  
 Ferguson, G. A.  
 Fisher, Henry  
 Fite, C. C. (A)  
 Frank, J. W.  
 Fries, H. H.  
 Fuller, G. W.  
 Garrigues, W. E.  
 Geisler, J. F.  
 Giddings, H. DeW.  
 Gies, W. J.  
 Godley, G. McM.  
 Goldman, A.  
 Goldstein, Harris (A)  
 Goodell, G. A.  
 Gruenberg, B. C.  
 Haigh, D. L.  
 Hall, R. W.  
 Hallock, A. P.  
 Hartford, James  
 Havemeyer, H. O.  
 Havens, F. S.  
 Haynes, D. O.  
 Hazen, Allen  
 Hesse, B. C.  
 Hicks, E. F.

## N MOUNTAIN.

Jes

## MANLIUS.

W. L.

## MECHANICSVILLE.

Griffin, M. L.

## MOUNT VERNON.

Blackmore, H. S.

## NEPERA PARK.

Baekeland, Leo

## NEW YORK CITY.

Adriance, J. S.  
 Alexander, Jerome  
 Allison, W. O. (A)  
 Alsop, W. K.  
 Amend, B. G.  
 Amend, O. P.  
 Ansbacher, L. A.  
 Arnott, G. W. C.  
 Austen, P. T.

NEW JERSEY (continued).  
 67  
 Fadle, Louis  
 Knorr, A. E.  
 Baker, Theodore  
 Pitman, J. R.  
 McCarty, L. W.  
 T. L.  
 RIDGEWOOD.  
 ROSELLE.  
 KISTIC.  
 FORD.

NEW YORK (*continued*).NEW YORK CITY (*continued*).

Hinckley, J. F.  
 Homer, C. S., Jr.  
 Huntington, Harwood  
 Huntington, S. V. V. (A)  
 Hyde, H. St. J.  
 Johnson, E. F.  
 Johnson, G. A.  
 Jones, W. A.  
 Kiessig, C. H. (A)  
 Kinsley, W. J. (A)  
 Kirchgasser, W. C.  
 Klein, O. H.  
 Kneeland, F. R.  
 Kruskal, Nicholas  
 Kuttroff, Adolph (A)  
 Lagai, G.  
 Lamar, W. R.  
 Lamborn, L. L.  
 Langmuir, A. C.  
 LeCl  ar, Thomas  
 Lederle, E. J.  
 Ledoux, A. R.  
 Levene, P. A.  
 Levine, E. J.  
 Loeb, Morris  
 Loomis, Horatio  
 Loos, H. A.  
 Love, E. G.  
 Macdowell, W. F.  
 Maitland, Alex. (A)  
 Matheson, W. J.  
 Matthiessen, F. O. (A)  
 McDowell, A. H.  
 McIlhiney, P. C.  
 McIntosh, Douglas  
 McKenna, C. F.  
 McLoughlin, Chas.  
 McMurtrie, Wm.  
 Mehrbach, Wm. (A)  
 Merz, Henry (A)  
 Meyer, G. M.  
 Meyer, Max  
 Miller, E. H.  
 Moody, H. R.  
 Moore, R. W.  
 Munsell, C. E.  
 Myers, J. A.  
 Neiman, H. S.  
 Neustadt, G. M. S.  
 Newman, J. W.  
 Nichols, W. H.  
 Oakes, F. J. (A)  
 Orth, A.  
 Parker, T. J.

NEW YORK CITY (*continued*).

Parmelee, C. W.  
 Peek, R. L.  
 Pellew, C. E.  
 Pfeiffer, C. H. (A)  
 Phillips, W. D.  
 Pitkin, Lucius  
 Poole, Herman  
 Prentice, W. P. (A)  
 Pretzfeld, C. J. (A)  
 Prochazka, G. A.  
 Prochazka, John  
 Renwick, E. S. (A)  
 Reubens, C. M. (A)  
 Reuter, L. H.  
 Rice, Charles  
 Richards, Edgar  
 Ricketts, P. de P.  
 Riggs, L. W.  
 Robeson, A. M. (A)  
 Roeser, Frederick  
 Rosell, C. A. O.  
 Rossi, A. J.  
 Ruhl, Louis (A)  
 Saarbach, Ludwig  
 Scheel, W. H. (A)  
 Scherr, E. W., Jr.  
 Schieffelin, W. J.  
 Schimpf, H. W.  
 Schnierwind, F.  
 Schroeder, Edward  
 Sch  pphaus, R. C.  
 Schweitzer, Hugo  
 Sherman, H. C.  
 Sloane, T. O'C.  
 Smith, Burnett (A)  
 Smith, E. E.  
 Sohon, M. D.  
 Soper, G. A.  
 Stebbins, J. H., Jr.  
 Steenken, J. C. (A)  
 Stern, Heinrich  
 Stillwell, C. M.  
 Stone, G. C.  
 St  rcke, H. E.  
 Stursberg, J. A. (A)  
 Sutro, H. H.  
 Takamine, Jokichi  
 Taylor, S. F.  
 Thatcher, C. J.  
 Tiffany, W. C.  
 Toch, M.  
 Trowbridge, M. L.  
 Trubek, Moses  
 Tucker, S. A.

NEW YORK (*continued*).NEW YORK CITY (*continued*).

Tuckerman, Alfred (A)

Uhlig, E. C.

Volney, C. W.

Von Herff, B.

Vulté, H. T.

Wainwright, J. H.

Waldstein, M. E.

Waller, Elwyn

Watters, L. L.

Wells, J. S. C.

Welt, Ida

Whitaker, M. C.

Wiechmann, F. G.

Wilkins, H. A. J.

Williamson, G. N.

Witthaus, R. A.

Woodcock, R. G.

Woodman, Durand

Wyatt, Francis

Yocum, J. H.

Youmans, W. J.

Zimmele, H. B.

## NIAGARA FALLS.

Doggett, C. S.

Escher, Paul

## OSWEGO.

Kingsford, T. P.

## POUGHKEEPSIE.

Harris, I. G.

Moulton, C. W.

## RICHMOND HILL.

Mar, F. W.

## ROCHESTER.

Davison, J. M.

Gallup, H. T.

Lattimore, S. A.

Wyckoff, G. H.

## NORTH CAROLINA.

## ASHEVILLE.

Fell, J. Wm.

Moale, P. R.

## CHAPEL HILL.

Baskerville, Charles

Howell, E. V.

Mills, J. E.

Pratt, J. H.

Venable, F. P.

## CHARLOTTE.

Hanna, G. B.

## SCHENECTADY.

Kessler, J. J., Jr.

## SYRACUSE.

Adgate, Matthew

Atwater, R. M.

Hazard, F. R.

Johnson, E. S.

Pattee, E. N.

Pennock, J. D.

Smith, H. M.

Spieler, A. J.

## TOTTENVILLE.

Hubbard, G. C. (A)

## TROY.

Coutie, Wm.

Mason, W. P.

Mittenzwey, Otto

Touceda, Enrique

## UTICA.

Hodges, G. C.

## WATERFORD.

Platt, E. S.

## WATERTOWN.

Schuyler, E. H.

## WEST ALBANY.

Voorhees, S. S.

## WHITESTONE.

Senff, C. H. (A)

## YONKERS.

Habirshaw, W. M.

Horne, W. D.

## DAVIDSON.

Martin, W. J., Jr.

## DURHAM.

Pegram, W. H.

## HICKORY.

Murrill, P. I.

## RALEIGH.

Asbury, S. E.

Bizzell, J. A.

Harris, C. D.

Haywood, W. G.

NORTH CAROLINA (*continued*).RALEIGH (*continued*).

Kilgore, B. W.  
 Pickel, J. M.  
 Syme, W. A.  
 Williams, C. B.  
 Withers, W. A.

## WAKE FOREST.

Brewer, C. E.

## WILMINGTON.

Ludlow, Gabriel

## NORTH DAKOTA.

## FARGO.

Ladd, E. F.

## OHIO.

## BELLEFONTAINE.

Butler, R. H. (A)

## CHILLICOTHE.

Watson, E. T.

## CINCINNATI.

Baker, D. H. (A)  
 Baringer, F. J.  
 Berghausen, E. J.  
 Berghausen, Oscar (A)  
 Campbell, Archibald  
 Corse, W. M.  
 Crane, W. H.  
 Dieckmann, Otto  
 Eichberg, J. H.  
 Ellms, J. W.  
 Evans, Thomas  
 Feid, G. F.  
 Fennel, C. T. P.  
 Finke, A. H. (A)  
 Fogetti, Lucien  
 Foote, H. B.  
 Hanson, C. A.  
 Harper, C. A.  
 Hawkins, C. C. (A)  
 Hochstetter, R. W.  
 Homburg, Fred.  
 Jones, A. O.  
 Joslin, C. E.  
 Lloyd, J. U.  
 Martin, O. W.  
 Meader, A. L. (A)  
 Merrell, C. G.  
 Mihalovitch, S. F. (A)  
 Morton, Cora  
 Newman, H. E.  
 Norton, T. H.  
 Ogilvy, D. J.  
 Pilhashy, B. M.  
 Porter, J. J. (A)  
 Proctor, R. W.  
 Pugh, A. H.

CINCINNATI (*continued*).

Ritchey, J. W.  
 Schmidt, Louis  
 Shepherd, F. I.  
 Simonson, Wm.  
 Springer, Alfred  
 Stadermann, A. L. (A)  
 Stephens, W. B.  
 Stern, David  
 Stierlin, E. (A)  
 Teasdale, W. S. (A)  
 Waldbott, Sigmund  
 Weber, Everhard  
 Weissmann, F. W.  
 Werk, Louis  
 Wessling, H. L.  
 Westenfelder, B. D.  
 Wetterstroem, T. D.  
 Wiborg, F. B.

## CLEVELAND.

Bragg, E. B.  
 Brush, C. F.  
 Burwell, A. W.  
 Crobaugh, F. L.  
 Franklin, A. I.  
 Graves, W. G.  
 Gronemeyer, H. H.  
 Gruener, Hippolyte  
 Hobbs, P. L.  
 Krause, A. H.  
 Lihme, I. P.  
 Mabery, C. F.  
 Morley, E. W. (Hon.)\*  
 Smith, A. W.  
 Textor, Oscar  
 Tower, O. F.  
 Worstall, R. A.

## COLUMBUS.

Bradford, Ernest  
 Fischer, Robert  
 Gore, H. C.

\* (Hon.) = Honorary Member.



OHIO (*continued*).COLUMBUS (*continued*).

Harrold, E. E.  
 Henderson, W. E.  
 Horton, E. G.  
 Howard, C. C.  
 Kohr, D. A.  
 Lord, N. W.  
 McPherson, Wm.  
 Somermeier, E. E.  
 Vinson, A. E.  
 Weber, H. A.

## DAYTON.

Elliott, Russell  
 Kittredge, H. G.

## DELAWARE.

Semans, W. O.

## GRAND RAPIDS.

Thurston, Azor

## HARTWELL.

Couch, G. E.

## HOME CITY.

Bosart, L. W., Jr.

## HORST.

Lanning, J. G. (A)

## LORAIN.

Du Pont, P. S.

## MADISONVILLE.

Driehaus, I. W. (A)

## MARLBORO.

Bloomfield, L. M.

## MINGO JUNCTION.

Ritchey, J. C.

## OBERLIN.

Chamberlain, J. S.

Jewett, F. F.

Taylor, T. M.

## OXFORD.

Hughes, R. M.

## PLEASANT RIDGE.

La Bach, J. O.

## SCIO.

Beal, J. H.

## SPRINGFIELD.

Linn, A. F.

## TOLEDO.

Hess, H. W.

Kirchmaier, G. A.

## UNION FURNACE.

Lovejoy, Ellis

## WYOMING.

Twitchell, E.

## YOUNGSTOWN.

Barrows, W. A., Jr.

Brinker, H. L.

## ZANESVILLE.

Langenbeck, Karl

## OKLAHOMA.

## STILLWATER.

Fields, John  
 Holter, G. L.

## OREGON.

## CORVALLIS.

Shaw, G. W.

## SALEM.

Tuthill, J. B. T.

## SUMPTER.

Redding, A. C.

## PENNSYLVANIA.

## ALLEGHENY.

Austin, N. M.  
 Fetterman, J. C.  
 Isaacs, A. S.  
 Lysle, W. S. (A)  
 Phillips, F. C.  
 Stifel, W. H. (A)

## ALLENTOWN.

Hartzell, H. S.

PENNSYLVANIA (*continued*).

<b>ALTOONA.</b>	<b>LANCASTER.</b>
Clements, F. O.	Beck, H. H.
Davis, R. S.	Schiedt, R. C.
Dudley, C. B.	<b>LANSDOWNE.</b>
McDonnell, M. E.	Dodge, F. E.
Pease, F. N.	<b>MT. ALVERNO.</b>
<b>BETHLEHEM.</b>	Barnett, E. S.
Richards, J. W.	<b>MUNHALL.</b>
<b>BERWICK.</b>	Wood, E. F.
Voorhees, G. E.	<b>NATRONA.</b>
<b>BRADDOCK.</b>	Hall, J. G.
Murray, C. B.	Heerlein, Robert
<b>BRYN MAWR.</b>	Kuntz, L. A.
Cushman, A. S.	McPetridge, Joseph
<b>CARLISLE.</b>	<b>OTTO.</b>
Lindsay, W. B.	Affelder, O. I.
Stephens, H. M.	<b>PHILADELPHIA.</b>
<b>CATASAUQUA.</b>	Armstrong, Theodore (A)
Louder, J. W. (A)	Atkinson, E. A.
<b>CHESTER.</b>	Attix, J. C.
Burt, M. C.	Auchy, George
Oglesby, W. R.	Barker, G. F.
<b>COATESVILLE.</b>	Benton, S. I.
Eachus, Charles	Blair, A. A.
Martin, H. G.	Boggs, G. H.
<b>CONSHOHOCKEN.</b>	Bower, W. H.
Clark, A. W.	Bradbury, R. H.
<b>DUQUESNE.</b>	Congdon, E. A.
Camp, J. M.	de Benneville, J. S.
<b>EASTON.</b>	Eavenson, Alban
Baker, J. T.	Ebaugh, W. C.
Church, H. K. (A)	Eckfeldt, J. B.
Hart, Edward	Genth, F. A.
Meade, R. K.	Glover, Henry
Schaffer, H. A.	Goldsmith, E.
Shimer, P. W.	Griffith, M. D.
Watson, H. E. G. (A)	Haines, Reuben
<b>ERIE.</b>	Hall, C. A.
Evans, J. A.	Hanna, D. C.
<b>ETNA.</b>	Hardin, W. L.
Calvert, J. E. (A)	Harold, J. F. X.
<b>FRANKLIN.</b>	Harrison, C. L. (A)
Conradson, P. H.	Hitchcock, F. R. M.
<b>HAVERFORD.</b>	Hooker, S. C.
Baxter, G. P.	Humphrey, R. L.
Hall, L. B.	Jayne, H. W.
<b>JOHNSTOWN.</b>	Jones, J. L.
Rising, H. R.	Kebler, L. F.
	Keller, H. F.
	Landis, E. K.
	LaWall, C. H.

PENNSYLVANIA (*continued*).PHILADELPHIA (*continued*).

Leffmann, Henry  
 Loos, E. A.  
 Lorenz, H. W. F.  
 Maas, Philip  
 Marshall, John  
 Matthews, J. M.  
 Meeker, G. L.  
 Moyer, J. B.  
 Neidich, S. A.  
 Oberholtzer, Vickers  
 Pemberton, Henry, Jr.  
 Pemberton, Ralph  
 Pennington, M. E.  
 Pierce, E. W.  
 Platt, Charles  
 Porter, Georgia  
 Pullman, F. C.  
 Remington, J. P.  
 Richards, Joseph  
 Rosengarten, G. D.  
 Rowland, W. L.  
 Sadtler, S. P.  
 Sadtler, S. S.  
 Schanche, H. G.  
 Schlichting, Emil  
 Seal, A. N.  
 Shinn, O. L.  
 Smith, E. F.  
 Snyder, O. J.  
 Starke, F. W.  
 Taggart, W. T.  
 Thomas, N. W.  
 Torrey, C. A., Jr.  
 Tuttle, D. K.  
 Tutwiler, C. C.  
 Whitfield, J. E.  
 Wood, J. R.

## PHOENIXVILLE.

Jameson, A. H.

## PITTSBURG.

Clapp, G. H.  
 Craig, A. G.  
 Craver, H. W.  
 Finley, N. H. (A)  
 Frohman, E. D.  
 Gearing, J. H. (A)  
 Gross, Abraham  
 Handy, J. O.  
 Hays, J. A.  
 Jones, A. B.  
 Keller, Charles  
 Kirk, D. M.  
 Mahon, R. W.

PITTSBURG (*continued*).

McTaggart, J. T.  
 Myers, H. E.  
 Phillips, W. B.  
 Stahl, K. F.  
 Waters, O. G. (A)  
 Wells, Allans

## READING.

Doolittle, O. S.  
 Faust, J. K.  
 Job, Robert  
 Sargent, G. W.

## SCRANTON.

Welles, A. H.

## SHARON.

Sanborn, E. R.

## SHARPSVILLE.

Dickson, W. E.

## SOUTH BETHLEHEM.

Buck, C. A.  
 Chandler, W. H.  
 Colby, A. L.  
 Drown, T. M.  
 Enright, Bernard  
 Schober, W. B.  
 Ullmann, H. M.

## SPRING FORGE.

Calkin, W. S.

## STATE COLLEGE.

Armsby, H. P.  
 Frear, Wm.  
 Fries, J. A.  
 Pond, F. J.  
 Pond, G. G.

## STEELTON.

Ellery, J. B.

## VANDERGRIFF.

Ginder, W. H. H.

## WASHINGTON.

Hamilton, L. P.

## WEST CHESTER.

Brinton, C. S. (A)  
 Cochran, C. B.  
 Roberts, C. C.

## WILKESBARRE.

Dean, W. H.

## YORK.

Ehrenfeld, C. H.

## RHODE ISLAND.

## KINGSTON.

Bucher, J. E.  
Hartwell, B. L.  
Washburn, J. H.  
Wheeler, H. J.

## NEWPORT.

Brown, H. F.  
Fullam, F. L.  
Gibbs, Wolcott (Hon.)  
Stevens, E. K.  
Tobin, J. J.  
Ziegler, J. C.

## OLNEYVILLE.

Saunders, W. M.

## PAWTUCKET.

Crocker, C. S.  
Fourniaux, E. A.  
Perry, C. M.

## PEACEDALE.

Jandrier, Edmond  
Sargent, C. L.

## PROVIDENCE.

Andrews, F. H.  
Andrews, G. F.  
Appleton, J. H.  
Arnold, N. D. (A)  
Breer, Louis  
Burgess, H. S. (A)  
Bush, C. S.  
Catlin, C. A.  
Farnsworth, J. P.  
Folsom, H. A.  
Fuller, R. C. (A)  
Hebden, J. C.  
Marlatt, A. L.  
Pearce, E. D.  
Perkins, G. E.  
Potter, C. A.  
Potter, W. R.  
Smith, W. E.  
Swett, C. E.  
Thayer, F. L.  
Woolworth, J. G.

## SOUTH CAROLINA.

## CHARLESTON.

Chazal, P. E.  
Miller, H. L.  
Parker, F. L.  
Reid, E. E.  
Robertson, Wm.

## CLEMSON COLLEGE.

Brackett, R. N.  
Hardin, M. B.  
Robertson, B. F.  
Shiver, F. S.

## SOUTH DAKOTA.

## DEADWOOD.

Dorr, J. V. N.  
Flintermann, R. F.  
Nicholls, G. A.

## RAPID CITY.

Slagle, R. L.

## TENNESSEE.

## BRISTOL.

Davis, W. W.  
Wilson, E. F.

## KNOXVILLE.

McBryde, J. B.  
Mooers, C. A.  
Wait, C. E.

## LEBANON.

Hinds, J. I. D.

## MOUNT PLEASANT.

Smither, F. W.

## NASHVILLE.

Brown, L. P.  
Dudley, W. L.  
Hollinshead, W. H.  
Kelley, J. H.  
McGill, J. T.

## TEXAS.

## AUSTIN.

Harper, H. W.

## EL PASO.

Seamon, W. H.  
Tuschka, Otto

## HOUSTON.

Sims, C. W.

## UTAH.

## MERCUR.

Fox, H. W.

## VERMONT.

## BURLINGTON.

Boynton, C. S.  
Merrill, N. F.  
Stearns, J. B.  
Torrey, H. A.

## MIDDLEBURY.

McGilton, W. W.  
Seely, H. M.

## NEWPORT.

Thrasher, E. C.

## VIRGINIA.

## BUENA VISTA.

Bolling, Randolph

## CHARLOTTESVILLE.

Dunnington, F. P.  
Mallet, J. W.

## EMORY.

Jarman, J. L.

## HOWARDSVILLE.

Logan, Lily

## LEXINGTON.

Howe, J. L.  
Pendleton, Hunter

## LONGDALE.

Meaker, W. L.

## LYNCHBURG.

Bowman, Walker.

## NORFOLK.

Cratty, J. M.

## PULASKI.

Daggett, W. W.

## RICHMOND.

Carpenter, F. B.  
Froehling, Henry  
Gaines, R. H.  
Hunter, J. R.  
Jones, C. C.  
Magruder, E. W.

## ROANOKE.

Anderson, Duncan, Jr.  
Sanders, C. N.

## WASHINGTON.

## INDEX.

Redding, C. R.

## NORTH YAKIMA.

McCurdy, C. W.

## PULLMAN.

Fulmer, Elton  
Heileman, W. H.

## REPUBLIC.

Lyng, M. H.

## SEATTLE.

Bogardus, C. E.

## SPOKANE.

Fassett, C. M.

## WEST VIRGINIA.

## BRAMWELL.

Wiley, W. B.

## MORGANTOWN.

Howard, C. D.

## WHEELING.

Bloch, J. A. (A)  
Bowman, J. W.  
Rawling, C. Q.  
Zimmer, H. W.

## WISCONSIN.

## Beloit.

Smith, E. G.

## MADISON.

Daniells, W. W.  
Hillyer, H. W.  
Kahlenberg, Louis

MADISON (*continued*).

Kremers, Edward  
Lenher, Victor  
Peppel, S. V.

## MAYVILLE.

Prentiss, G. N.

WISCONSIN (*continued*).

## MILWAUKEE.

Baumgarten, F. M.  
MacPherran, R. S.  
Mitchell, A. S.  
Smith, H. F.

## OSHKOSH.

Goddard, H. N.

## RACINE.

Hindley, R. C.

## MINERAL POINT.

Chase, M. F.  
Mackay, P. A.

## WYOMING.

## ENCAMPMENT.

Eberman, W. S.

## LARAMIE.

Slosson, E. E.

## PUERTO RICO.

## SAN JUAN.

Berkeley, W. N.

## HAWAIIAN ISLANDS.

Maxwell, Walter  
Shorey, E. C.  
Thompson, Firman

## FOREIGN COUNTRIES.

## AFRICA.

Quinan, W. R.

## CHILI.

Mathewson, E. P.

## AUSTRALIA.

Steel, F. W.

## CHINA.

Lyman, E. R.

## BARBADOES.

Thorne, E. E. H.

## CUBA.

Cuadrado, G. A.  
Fernandez-Cavada, F. (A)  
Muñoz, L. E.  
Whitaker, DeBerniere

## BRITISH GUIANA, S. A.

Douglas, Wm.  
Harrison, J. B.  
Kauffmann, W. P.

## ENGLAND.

Armstrong, H. E.  
Crookes, Sir William (Hon.)  
Elworthy, H. S.  
Jones, F. W.  
Power, F. B.  
Redwood, Boverton  
Rhodes, Edward  
Stead, J. E.  
Stillwell, J. S.  
Tyrer, Thomas  
Williamson, A. W. (Hon.)

## CANADA.

Andrews, W. W.  
Archibald, E. H.  
Carlsson, Hugo  
Guess, H. A.  
Harrington, B. J.  
James, J. H.  
Johnson, J. F.  
Macfarlane, Thomas  
McFarlen, T. J.  
Miller, W. L.  
Morgan, T. M.  
Neish, A. C.  
Roller, H. C. (A)  
Shuler, D. P.  
Shutt, F. T.  
Shuttleworth, A. E.  
Thomas, W. H., Jr.

## FRANCE.

Berthelot, M. (Hon.)  
Chalon, P. F.  
Moissan, Henri (Hon.)

FOREIGN COUNTRIES (*continued*).

## GERMANY.

Browne, C. A., Jr.  
 Pahlberg, Constantin  
 Harding, E. P.  
 Krause, G.  
 Ostwald, Wilhelm (Hon.)  
 Sauer, Ewald  
 Sternberg, L.  
 van't Hoff, J. H. (Hon.)  
 Wallenstein, Florian

## ITALY.

Cannizzaro, Stanislao (Hon.)

## JAVA.

Boot, J. C.

## MEXICO.

Brown, Thomas, Jr.  
 Garduño, Jesus  
 Harms, Armin  
 Hough, G. J.  
 Keller, Cornelius  
 Schloss, J. A.  
 Wardman, G. B.

## RUSSIA.

Bregowsky, I. M.  
 Mendeléeff, D. (Hon.)

## SCOTLAND.

Dobbin, Leonard  
 Longstaff, J. P.  
 Macadam, W. I.  
 Martin, A. M.  
 Pinkerton, D. J.

## SUMMARY BY STATES.

Alabama .....	13	New Hampshire .....	12
Arizona .....	6	New Jersey .....	97
Arkansas .....	2	New Mexico .....	1
California .....	44	New York... ..	356
Colorado .....	10	North Carolina .....	22
Connecticut .....	28	North Dakota .....	1
Delaware .....	4	Ohio .....	111
District of Columbia .....	72	Oklahoma .....	2
Florida .....	3	Oregon .....	3
Georgia .....	12	Pennsylvania .....	166
Idaho .....	2	Rhode Island .....	37
Illinois .....	83	South Carolina .....	9
Indiana .....	14	South Dakota .....	4
Iowa .....	9	Tennessee .....	12
Kansas .....	13	Texas .....	4
Kentucky .....	8	Utah .....	1
Louisiana .....	11	Vermont .....	7
Maine .....	10	Virginia .....	19
Maryland .....	28	Washington .....	7
Massachusetts .....	208	West Virginia .....	6
Michigan .....	48	Wisconsin .....	16
Minnesota .....	19	Wyoming .....	2
Mississippi .....	4	Puerto Rico .....	1
Missouri .....	21	Hawaii .....	3
Montana .....	22	Foreign Countries .....	68
Nebraska .....	16		
Nevada .....	2		
		Total .....	1679

## GENERAL MEETINGS.

1. Newport, R. I., August 6 and 7, 1890.
2. Philadelphia, Pa., December 30 and 31, 1890.
3. Washington, D. C., August 17 and 18, 1891.
4. New York, N. Y., December 29 and 30, 1891.
5. Rochester, N. Y., August 16 and 17, 1892.
6. Pittsburg, Pa., December 28 and 29, 1892.
7. Chicago, Ill., August 21 and 22, 1893.
8. Baltimore, Md., December 27 and 28, 1893.
9. Brooklyn, N. Y., August 15 and 16, 1894.
10. Boston and Cambridge, Mass., December 27 and 28, 1894.
11. Springfield, Mass., August 27 and 28, 1895.
12. Cleveland, O., December 30 and 31, 1895.
13. Buffalo, N. Y., August 21 and 22, 1896.
14. Troy, N. Y., December 29 and 30, 1896.
15. Detroit, Mich., August 9 and 10, 1897.
16. Washington, D. C., December 29 and 30, 1897.
17. Boston, Mass., August 22 and 23, 1898.
18. New York, N. Y., December 28 and 29, 1898.
19. Columbus, O., August 21 and 22, 1899.
20. New Haven, Conn., December 27 and 28, 1899.
21. New York, N. Y., June 25 and 26, 1900.











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